

## **APPENDIX G**

### **Geochemistry Calculations**

- G.1, Water-Type Calculation Methods
- G.2, Environmental Occurrence and Chemistry of Metals of Potential Concern
- G.3, Estimation of Distribution Coefficients ( $K_D$ ) for Lead, Zinc, and Cadmium in the Coeur d'Alene River Basin
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## **G.1**

### **WATER-TYPE CALCULATION METHODS**

## **G.1, WATER-TYPE CALCULATION METHODS**

Waters in the western portion of the United States (west of the Mississippi) are often in equilibrium with calcium carbonate (also known as calcite or  $\text{CaCO}_3$ ). Calcium carbonate can readily precipitate from solution if the pH of the water increases or if the temperature of the water rises. Contrary to most minerals, calcium carbonate has a lower solubility at higher temperatures (retrograde solubility). Computations of carbonate and bicarbonate from pH and alkalinity and calcite precipitation are discussed below.

### **Chemical Data Requirements**

The minimum data set that should be collected is alkalinity, pH, and dissolved iron and calcium concentrations. The pH should be a field pH as pH is temperature dependent and degassing will cause pH changes. In addition to alkalinity, pH, and calcium concentrations, it is desirable to measure the temperature, and the total dissolved solids. With proper tools (e.g., geochemical models) it is advantageous to have ions that affect ionic strength and ions that pair significantly in addition to ions of interest. However, ion pair formation is not considered in the spreadsheet. Data needs for the spreadsheet are summarized below:

- Alkalinity (mg/L  $\text{CaCO}_3$ )
- pH (units)
- Total calcium concentration
- Temperature
- Total dissolved solids (TDS); alternatively, one may use EC (electrical conductivity, see Eq. 5)

### **Computation of Carbonate and Bicarbonate and Calcite Saturation Index**

The objective of this section is to detail the steps that the spreadsheet goes through to compute the degree of calcite equilibrium with a groundwater and the concentrations and activities of carbonate and bicarbonate. The carbonate and bicarbonate numbers were used in the Piper diagrams to plot waters types with the Coeur d'Alene basin.

The variances, of the solubility product ( $K_{sp}$ ) for calcite and first ( $K_1$ ) and second ( $K_2$ ) dissociation constants for carbonic acid, with temperature, are computed by the method of Plummer and Busenberg (1982):

$$\text{Log } K_{sp} = -171.9065 - 0.077993T_k + 2839.319/T_k + 71.595 \log T_k \quad \text{Eq. 1}$$

$$\text{Log } K_1 = -356.3094 - 0.06091964T_k + 21,834.37/T_k + 126.8339 \log T_k - 1,684,915/T_k^2 \quad \text{Eq. 2}$$

$$\text{Log } K_2 = -107.8871 - 0.03252849T_k + 5151.79/T_k + 38.92561 \log T_k - 563713.9/T_k^2 \quad \text{Eq. 3}$$

where:

$$T_k = 273.15 + T^\circ\text{C} \quad \text{Eq. 4}$$

and  $T_k$  is the temperature in degrees Kelvin while  $T^\circ\text{C}$  is the temperature in degrees Centigrade. These corrections are good over the temperature range of  $0^\circ\text{C}$  to  $100^\circ\text{C}$ .

The ionic strength of the solution is computed by combining equations 5 and 6 (Griffin and Jurinak 1973) and arriving at equation 7:

$$\text{TDS} = 640 \text{ EC} \quad \text{Eq. 5}$$

$$I = 0.0127 \text{ EC} \quad \text{Eq. 6}$$

$$I = \text{TDS}/50,394 \quad \text{Eq. 7}$$

where:

TDS = total dissolved solids (mg/L)  
 EC = electrical conductivity (mmhos/cm)  
 I = ionic strength (moles/L)

The activity coefficient (f) is calculated by:

$$-\log f = AZ^2 [(I^{1/2}/(1 + I^{1/2}) - 0.3I] \quad \text{Eq. 8}$$

Thus, monovalent activity coefficients ( $f_m$ ) are computed by:

$$f_m = 10^{-[(A \cdot I/2)/(1+I/2)] - 0.3I} \quad \text{Eq. 9}$$

and divalent activity coefficients ( $f_d$ ) are calculated by:

$$f_d = f_m^4 \quad \text{Eq. 10}$$

The temperature dependence of the "A" constant is given by:

$$1.82 \times 10^6 (E \cdot T_k)^{-1.5} \quad \text{Eq. 11}$$

where E is the dielectric constant computed from:

$$E = [60,954/(T_k + 116)] - 68.937 \quad \text{Eq. 12}$$

Next, we use the alkalinity to compute the concentration and then the activity of the carbonate ion. Total alkalinity is calculated by titration to a pH of approximately 4.5, the methyl orange endpoint. Equation 13 contains the definition of alkalinity.

$$\text{Alkalinity (meq/L)} = 1 \text{ meq/mmol} \times \text{MHCO}_3^- + 2 \text{ meq/mmol} \times \text{MCO}_3^{2-} \quad \text{Eq. 13}$$

where:

$\text{MHCO}_3^-$  and  $\text{MCO}_3^{2-}$  represent the concentrations of the bicarbonate and carbonate ions, respectively

This equation assumes that all the alkalinity is bicarbonate/carbonate, i.e., other titratable anions (e.g.,  $\text{H}_3\text{SiO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{OH}^-$ , organic anions) are not present in significant quantities.

Using the second acidity constant of carbonic acid dissociation:

$$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+ \text{ with an equilibrium constant of } 10^{-10.3} \quad \text{Eq. 14}$$

By placing the products over the reactants we have:

$$(\text{ACO}_3^{2-} \cdot \text{AH}^+)/\text{AHCO}_3^- = 10^{-10.3} \quad \text{Eq. 15}$$

where A = activity of ion.

Rearranging:

$$\text{ACO}_3^{2-} = (10^{-10.3} \text{AHCO}_3^-)/\text{AH}^+ \quad \text{Eq. 16}$$

$$\text{AHCO}_3^- = (\text{ACO}_3^{2-} \text{AH}^+)/10^{-10.3} \quad \text{Eq. 17}$$

Substituting equation 17 into equation 13 and assuming that the  $\text{ACO}_3^{2-}$  is equal to  $\text{MCO}_3^{2-}$  we have:

$$\text{Alkalinity (meq/L)} = (\text{MCO}_3^{2-} \text{AH}^+)/10^{-10.3} + 2\text{MCO}_3^{2-} \quad \text{Eq. 18}$$

$$= \text{MCO}_3^{2-} (\text{AH}^+/10^{-10.3} + 2) \quad \text{Eq. 19}$$

$$\text{MCO}_3^{2-} = \text{Alkalinity (meq/L)} / (\text{AH}^+/10^{-10.3} + 2) \quad \text{Eq. 20}$$

$$\text{Alkalinity (mg/L CaCO}_3\text{)}/50 \text{ mg/meq} = \text{Alkalinity (meq/L)} \quad \text{Eq. 21}$$

Substituting equation 21 into equation 20 we arrive at:

$$\text{MCO}_3^{2-} \text{ (mmole/L)} = [\text{Alkalinity (mg/L CaCO}_3\text{)}/50 \text{ mg/meq}] / (\text{AH}^+/10^{-10.3} + 2) \quad \text{Eq. 22}$$

To convert from mmole/L to mg/L we multiply by 60 as shown in equation 23:

$$\text{MCO}_3^{2-} \text{ (mg/L)} = \text{MCO}_3^{2-} \times 60 \text{ mg/mmole} \quad \text{Eq. 23}$$

To convert mmoles/L to moles per liter we divide by 1,000.

Concentrations are converted to activities by:

$$A = fM \quad \text{Eq. 24}$$

where:

A and M are previously defined and f is the activity coefficient or fugacity.

To compute the saturation index (S.I.) we compute the activities of the bare calcium two ions ( $\text{Ca}^{2+}$ ) and the bare  $\text{CO}_3^{2-}$  ions. We next compute an activity product (AP) by multiplying the activity of the bare calcium ion by the activity of the bare carbonate ion (Eq. 25). We then compute a S.I. by taking placing the log of the activity product over the solubility product and taking the log of the activity product over the solubility product as in equation 26 below.

$$A\text{CO}_3^{2-} \times A\text{Ca}^{2+} = \text{AP} \quad \text{Eq. 25}$$

$$\text{Saturation index (S.I.)} = \log[(\text{AP})/(\text{SP})] \quad \text{Eq. 26}$$

where:

AP = activity product  
SP = solubility product  
S.I. = saturation index

Knowing the S.I. we can determine whether the groundwater is currently oversaturated, in equilibrium, or undersaturated with calcite as indicated below.

S.I. > 0 calcite is oversaturated and will precipitate from solution  
S.I. = 0 calcite is in equilibrium and will precipitate if the pH rises  
S.I. < 0 calcite is undersaturated and will not precipitate unless the pH rises sufficiently

In geochemical modeling S.I.s within + or – 5 percent of the log of the solubility product are considered to be in equilibrium with a particular solid or mineral. The solubility product for calcite at 25°C is  $10^{-8.48}$ . Using our equilibrium criterion, if we compute a S.I. between + or – 0.42 for calcite, the calcite is considered to be in equilibrium with the groundwater.

Alternatively, the S.I. can be computed by correcting the solubility product for ionic strength as shown below:

$$K_{\text{spc}} = K_{\text{sp}}/f_d^2 \quad \text{Eq. 27}$$

where:

$K_{\text{spc}}$  is the solubility product ( $K_{\text{sp}}$ ) for calcite corrected for ionic strength.

Saturation indices (S.I.s) are computed both ways in the spreadsheet. First, using the activities for calcium and carbonate and, second, using the solubility product corrected for ionic strength. Obviously, the two S.I.s should be exactly the same.



## REFERENCES

- Griffin, R.A. and J.J. Jurinak. 1973. "Estimation of Activity Coefficients From the Electrical Conductivity of Natural Aquatic Systems and Soil Extracts." *Soil Science* 116:26-30.
- Plummer, L.N. and E. Busenberg. 1982. *The Solubilities of Calcite, Aragonite and Vaterite in CO<sub>2</sub>-H<sub>2</sub>O Solutions Between 0 and 90°C, and an Evaluation of the Aqueous Model of the System CaCO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O*. *Geochemica et Cosmochimica Acta*, Vol. 46: pp. 1011-1040.

## **G.2**

### **ENVIRONMENTAL OCCURRENCE AND CHEMISTRY OF METALS OF POTENTIAL CONCERN**

## **G.2, ENVIRONMENTAL OCCURRENCE AND CHEMISTRY OF METALS OF POTENTIAL CONCERN**

### **INTRODUCTION**

In this section, contaminants of potential concern (lead, zinc, cadmium, iron, arsenic, manganese, mercury, copper, silver, and antimony) are discussed in terms of their environmental occurrence in general and within the Coeur d'Alene River basin. Sources used for the environmental occurrences of various metals in the Coeur d'Alene River basin are limited in this section. The intent of this section is to provide an overview of metal concentrations and chemistry. Further, the aqueous species, solid phases and adsorption reactions expected to be found in the Coeur d'Alene River basin are discussed.

Lead, zinc, cadmium, iron, and arsenic are discussed in some detail because they are considered to significantly impact water quality in the Coeur d'Alene River basin. Lead, zinc, and cadmium are discussed in more detail because large areas of the Coeur d'Alene River basin contain waters with exceedances of water quality criteria of these metals. Iron is also discussed in some detail because of its role in the fate and transport of other metals. Arsenic is examined because of its toxicity and known association with the other metals in ore bodies. Further, arsenic is important because of its potential for desorption from soil and iron surfaces in the presence of phosphate. Phosphate minerals have been identified as potentially important in passive treatment of discharges from adits, tailings piles and seeps.

For other inorganic elements that occur in the Coeur d'Alene River basin, such as mercury, copper, manganese, silver, and antimony only a cursory discussion is provided because few exceedances of water quality criteria have been observed for these elements. Accordingly, they are less important to the regional geochemistry of the Coeur d'Alene River basin.

### **LEAD (Pb)**

#### **Environmental Occurrence**

Geochemical "background concentrations" of lead have been reported to vary from 10 to 20 mg/kg (Sauve et al. 1993). However, most industrialized societies have soil concentrations higher than this because of anthropogenic activities. Dragun (1988) states that typical lead

concentrations in soil range from 2.0 to 200 mg/kg while Lindsay (1979) reports an average value of 10 mg/kg.

In the natural resource damage assessment (NRDA) report prepared by the Trustees (Stratus 1999), baseline concentrations for floodplain soils and sediments, and bed, bank, and suspended sediments were developed collectively. The baseline lead concentration for soils or sediments was stated to be 30 mg lead/kg on a dry weight basis. For the Coeur d'Alene River basin, the median and 90th percentile values for lead in uncontaminated soil studied by Gott and Cathrall (1980) were 43 and 171 mg/kg, respectively. Gott and Cathrall (1980) also calculated the median (19) and 90th percentile (140) concentrations for lead in rock.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved lead in the upper South Fork were 0.17 and 1.11  $\mu\text{g/L}$ , respectively. In the Page-Galena mineral belt the respective concentrations were 0.54 and 0.98  $\mu\text{g/L}$ . The corresponding values in the Pine Creek drainage were 0.21 and 0.41  $\mu\text{g/L}$ . Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for dissolved lead was 0.21  $\mu\text{g/L}$  and the 95th percentile value was 1.09  $\mu\text{g/L}$ .

## **Environmental Chemistry**

### ***Aqueous Species***

Naturally occurring lead primarily is found in the +2 oxidation state. Under given conditions ( $\text{Pb}^{2+}$  activity fixed at  $10^{-7}$  molar or controlled by cerussite ( $\text{PbCO}_3$ ),  $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$  molar, and  $\text{CO}_2 =$  atmospheric conditions ( $10^{-3.52}$  atmospheres), Rai and Zachara 1986), the  $\text{Pb}^{2+}$  species dominates under acidic ( $\text{pH} < 7$ ) conditions followed by the  $\text{PbSO}_4^0$  species. Under alkaline conditions, carbonate anions form strong complexes with lead with the  $\text{PbCO}_3^0$  species dominant up to a pH of approximately 9 after which  $\text{Pb}(\text{CO}_3)_2^{2-}$  is the principal solution species. The majority of the pH values recorded in the Coeur d'Alene River basin are found in the pH range of 5 to 7 with a smaller number of samples in the pH range of 7 to 8. Consequently, it is anticipated that predominant solution species of lead found in groundwaters and surface waters of the Coeur d'Alene River basin will be the  $\text{Pb}^{2+}$  and  $\text{PbSO}_4^0$  species with the  $\text{Pb}^{2+}$  species the major species except under relatively high sulfate concentrations. The  $\text{PbCO}_3^0$  species is expected to be the major species in the Coeur d'Alene River basin under conditions ( $\text{pH} > 7$ ) highly buffered by the dissolution of carbonate deposits.

### ***Adsorption***

As manifested by lead associated with particulates found in waters throughout the Coeur d'Alene River basin, lead is strongly retained by soil and metal oxide adsorbents through ion exchange and specific adsorption reactions, respectively. There is a strong positive correlation between the clay and organic matter content of soils and lead adsorption. Because of the predominance of the  $Pb^{2+}$  species below a pH of approximately 7, lead is expected to strongly compete for ion exchange sites on clays, particularly above a pH of approximately 4.6 as this is higher than the typical point of zero charge of clays. For example, the point of zero charge of montmorillonite occurs, approximately, at a pH value of 4.6. Therefore, above this pH value montmorillonite will have a net negative charge and below this pH it will have a net positive charge. Lead is expected to adsorb strongly onto clays at the pH values typically found in the Coeur d'Alene River basin (5 to 8).

It has been persuasively argued by Lee (1975) that colloidal forms of iron oxyhydroxides may be the most significant sink for lead in the environment. Correlations between lead and iron oxyhydroxides in the Coeur d'Alene River basin and adsorption modeling are discussed in Section G-3. Lead demonstrates a particularly strong affinity for iron oxides, with the order of adsorption being  $Pb^{2+} > Cd^{2+} > Zn^{2+} > Ca^{2+} > K^{+}$  (Lee 1975). Iron is found in high concentrations in ore bodies throughout the Coeur d'Alene River basin. Iron oxyhydroxide precipitates are known to sequester lead from mine leachates (Davis et al. 1999; Peterson et al. 1982; Serne et al. 1983). Adsorption of metal cations onto oxide surfaces is highly pH dependent with the adsorption going from zero to 100 percent over a narrow pH range, typically from one to two pH units. As the adsorbate/adsorbent ratio decreases there is a shift in the adsorption edge of cations to the left. That is, more adsorption will occur at lower pH values as we decrease the amount of adsorbate or increase the quantity of adsorbent. At a solution iron concentration of approximately 60 mg/L and a lead concentration of approximately 1.0 mg/L, close to 100 percent lead adsorption will take place at a pH of approximately 6.5 or higher. Decreasing lead adsorption occurs with decreasing pH until a pH of approximately 3.0, where no lead adsorption occurs. Thus, permeable reactive barriers in the Coeur d'Alene River basin using lead removal by iron oxyhydroxides should ensure a pH value of at least 6.5. Little lead will adsorb onto iron oxyhydroxides at pH values less than 4 except at higher dissolved iron/lead ratios (e.g., iron/lead ratios of 200:1 or higher).

Dragun (1988) reports observed lead  $K_d$  values ranging from 4.5 to 7,640 mL/g with a mean\* value of approximately 100. For the pH range of 5 to 9, Strenge and Peterson (1989) selected representative values to use in modeling studies of 234 to 1,830 mL/g, depending on the soil

composition. Adsorption coefficients ( $K_d$  values) for collocated water and soil samples in the Coeur d'Alene River basin are presented in Appendix G.3.

### ***Solid Phase***

Studies of uranium mill tailings (Peterson and Krupka 1981; Peterson et al. 1982) suggested that anglesite ( $\text{PbSO}_4$ ) could be in equilibrium with uranium mill tailings after contact with clay and other geologic materials. However, in their work, adsorption onto hydrous iron oxides appeared to be the predominant mechanism controlling solution concentrations of lead. Based on the sulfate activities computed for uranium mill tailings solutions percolated through permeability columns (Peterson et al. 1982), the lead concentrations maintained in solution by anglesite would be relatively high (600  $\mu\text{g/L}$ ) and significantly above the EPA established drinking water standard. Anglesite is expected to form in the Coeur d'Alene River basin near ores where pyrite oxidation occurs.

Serne et al. (1983) found that radiotraced lead was more strongly retained than other transition metals and tied up in the upper portions of the columns. The semi-selective extraction data (Serne et al. 1983) indicated that  $^{210}\text{Pb}$  was predominantly associated with crystalline or amorphous iron and aluminum oxides, with some Pb being exchangeable. Because  $^{210}\text{Pb}$  remained immobilized, even after the soil's initial buffering capacity had been exhausted and iron oxides began to redissolve, lead appeared to be immediately bound to cation exchange sites or to other soil minerals upon dissolution of the iron oxides.

Ma et al. (1993) speculated that hydroxypyromorphite was precipitating from solution and controlling lead concentrations at low levels when hydroxyapatite ( $\text{Ca}_5[\text{PO}_4]_3\text{OH}$ ) was applied to Pb in aqueous solution, on exchange resins and in soil. In this work, application of hydroxyapatite reduced lead concentrations from 5 to 500 mg/L down to 0.18 to 19.7  $\mu\text{g/L}$ .

In summary, theoretical and experimental evidence indicates that lead phosphates are the most stable and insoluble forms of lead when sufficient phosphate is present. This has application to the construction of permeable reactive barriers to treat leachates from adits, tailings piles, and seeps in the Coeur d'Alene River basin. Under high sulfate concentrations commonly found in oxygenated seepage waters from mine adits, tailings and waste piles, anglesite ( $\text{PbSO}_4$ ) may precipitate from solution in the absence of sufficient phosphate and control solution concentrations of lead. Lead carbonates and hydroxides are also possible controls on lead concentrations but generally are not expected to control lead concentrations at pH values found in most waters within the Coeur d'Alene River basin. Galena (lead sulfide) will form under very

reducing conditions and this mineral is found in ores throughout the Coeur d'Alene River basin. Under reducing conditions, galena will control the activity of lead in solution.

## **ZINC (Zn)**

### **Environmental Occurrence**

Zinc concentrations encountered in soils generally range from 10 to 300 mg/kg (Dragun 1988) with an average of 50 mg/kg (Lindsay 1979).

In the NRDA report prepared by the Trustees (Stratus 1999), baseline concentrations for floodplain soils and sediments, and bed, bank, and suspended sediments were developed collectively. The baseline concentration for soil and sediment was stated to be 63 mg zinc/kg dry weight of soil or sediment. For the Coeur d'Alene River basin, the median and 90th percentile values for zinc in soil studied by Gott and Cathrall (1980) were 95 mg/kg and 280 mg/kg, respectively. Gott and Cathrall (1980) also calculated the median (36 mg/kg) and 90th percentile (130 mg/kg) concentrations for zinc in rock from throughout the Coeur d'Alene River basin.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved zinc in the upper South Fork were 6.13 and 24.37 µg/L, respectively. In the Page-Galena mineral belt the respective concentrations were 12.00 and 76.92 µg/L. The corresponding values in the Pine Creek drainage were 3.13 and 8.79 µg/L. Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for dissolved zinc was 6.13 µg/L and the 95th percentile value was 71.67 µg/L.

### **Environmental Chemistry**

#### ***Aqueous Species***

Under natural aqueous conditions, zinc is found exclusively in the +2 oxidation state. Given an assumed groundwater composition ( $\text{Zn}_2\text{SiO}_4$ , willemite, solid-phase control, activity  $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$ ,  $\text{CO}_2 = 10^{-3}$  atmospheres; Rai and Zachara 1986), the dominant Zn species in solution at pH values less than 8.2 is  $\text{Zn}^{2+}$ . Under these assumed conditions, the  $\text{ZnSO}_4^0$  neutral ion pair is only slightly less soluble than the  $\text{Zn}^{2+}$  species. Above a pH value of 8.2, the  $\text{Zn}(\text{CO}_3)_2^{2-}$  species is

predominant. Therefore, the  $\text{Zn}^{2+}$  species is expected to be the major aqueous species found throughout the Coeur d'Alene River basin.

### ***Adsorption***

Similarly to other cationic heavy metals, the adsorption of zinc occurs through ion exchange reactions and by specific adsorption onto metal oxide surfaces. Specific adsorption tends to prevail at low concentrations of zinc while cation exchange occurs when metal oxide sites governed by specific adsorption are saturated. Lindsay (1979) has attributed the solubility of zinc in soils to a soil-Zn adsorption equilibrium and has, moreover, developed an expression (Equation 16) to predict aqueous zinc concentrations in soils.

$$\log [\text{Zn}^{2+}] = 5.8 - 2\text{pH} \quad (16)$$

where zinc concentrations,  $[\text{Zn}^{2+}]$ , are expressed in mole/L.

Based on this relationship, at a pH value (6.0) commonly found in waters of the Coeur d'Alene River basin, the concentration of  $\text{Zn}^{2+}$  in solution would be approximately 41  $\mu\text{g/L}$ . This concentration is below aqueous zinc values often found in soil pore water in the Coeur d'Alene River basin and, therefore, it does not appear that soil-Zn is controlling zinc concentrations in most of the basin.

Adsorption onto iron and manganese oxides has been postulated to be the predominant mechanism controlling zinc concentrations in soils (Balistieri and Murray 1982; Kinniburgh and Jackson 1982). Peterson et al. (1983) and Serne et al. (1983) concluded from column studies and semi-selective extraction data that to accurately and quantitatively account for the migration of zinc, one must take into consideration its pH dependent immobilization onto precipitated hydrous oxides and other phases already present in the columns. Divalent alkaline earth cations, such as those found in the Coeur d'Alene River basin due to carbonate dissolution (e.g.,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), will compete with  $\text{Zn}^{2+}$  for adsorption sites on soils (Shukla et al. 1980) and iron oxides (Dzombak 1986) at high concentrations ( $>10^{-3}$  mol or approximately 400 mg/L calcium). Aqueous calcium concentrations this high are not commonly found in the Coeur d'Alene River basin and are only expected to exist at the interface between an acid front and carbonate minerals. Conversely, ionic strength and anions were shown to have no effect on zinc adsorption on two soils (Shuman 1986). Zinc adsorption onto amorphous iron oxyhydroxides is negligible below a pH of 4.0. Adsorption increases with increasing pH until at a pH value of approximately 6.0 to 7.0, 100 percent adsorption occurs. The exact location and shape of the pH adsorption curve depend on the specific concentrations of iron and zinc and background electrolytes.



There is a wide range of zinc  $K_d$  values reported in the literature. These values range from 0.1 to 8,000 mL/g (Dragun 1988) with a mean value of 16.4. Values ranging from 13.0 to 1,460 mL/g for the pH range of 5 to 9 were selected by Streng and Peterson (1989). This pH range should be of most interest in studying adsorption in the Coeur d'Alene River basin. Adsorption coefficients ( $K_d$  values) for collocated water and soil samples in the Coeur d'Alene River basin are presented Appendix G.3.

### ***Solid Phases***

Thermodynamic equilibrium relationships were insufficient to characterize the movement of zinc in column studies conducted with uranium mill tailings solutions and soils (Peterson et al. 1983). Lindsay (1979) has speculated that franklinite ( $ZnFe_2O_4$ ) in equilibrium with Fe(III) controls solution concentrations of zinc. Jenne et al. (1980) thought that willemite or perhaps a zinc carbonate controlled zinc concentrations in waters sampled near zinc and lead mines. However, both franklinite and willemite are high-temperature solids and would not be expected to form in sediment/solution interactions. Other zinc minerals, such as  $Zn(OH)_2$ , ZnO (zincite), and  $ZnCO_3$  (smithsonite) normally are too soluble to control zinc concentrations being approximately  $10^5$  times more soluble than soil-Zn. However, given the high zinc concentrations found in certain locations within the Coeur d'Alene River basin, these solids may be important in isolated areas. Sphalerite ( $ZnS$ ) forms under low redox potentials and will control zinc concentrations under anaerobic conditions. Ores containing this mineral are found throughout the Coeur d'Alene River basin.

In summary, it initially appears that adsorption reactions and not solid or mineral phases are controlling the solution concentrations of zinc with the exception of sphalerite under anaerobic conditions. However, Hinz and Selim (1994) were unsuccessful in using isotherm and ion exchange reactions to describe the transport of zinc and cadmium in soils. Additionally, high solution concentrations of zinc may lend themselves to solid-phase controls.

## **CADMIUM (Cd)**

### **Environmental Occurrence**

Lindsay (1979) reports that the common concentration range for cadmium in soils is 0.01 to 0.70 mg/kg with an average concentration of 0.06 mg/kg. In the NRDA report prepared by the Trustees (Stratus 1999), baseline concentrations for floodplain soils and sediments, and bed, bank, and suspended sediments were developed collectively. The baseline concentration for soils

or sediments was stated to be 0.61 mg cadmium/kg of soil or sediment on a dry weight weight basis. For the Coeur d'Alene River basin, the median and 90th percentile values for cadmium in soil studied by Gott and Cathrall (1980) were 0.8 mg/kg and 2.7 mg/kg, respectively. Gott and Cathrall (1980) also calculated the median (0.4 mg/kg) and 90th percentile (1.1 mg/kg) concentrations for cadmium in rock from throughout the Coeur d'Alene River basin.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved cadmium in the upper South Fork were 0.06 and 0.20  $\mu\text{g/L}$ , respectively. In the Page-Galena mineral belt the respective concentrations were 0.17 and 0.84  $\mu\text{g/L}$ . The corresponding values in the Pine Creek drainage were 0.12 and 0.25  $\mu\text{g/L}$ . Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for dissolved cadmium was 0.08  $\mu\text{g/L}$  and the 95th percentile value was 0.78  $\mu\text{g/L}$ .

## **Environmental Chemistry**

### ***Aqueous Species***

Cadmium exists only in the +2 oxidation state in aqueous solutions. With a cadmium activity maintained by  $\text{CdCO}_3$  (otavite) and sulfate activity fixed at  $10^{-3}$  M, the dominant aqueous species is  $\text{Cd}^{2+}$  at pH values  $<8.2$  ( $\text{PCO}_2$  fixed at  $10^{-3.53}$ ). The activity of  $\text{CdSO}_4^0$  under this pH regime ( $<8.2$ ) is approximately one-half log unit lower than that of  $\text{Cd}^{2+}$  and is the second most dominant species. The  $\text{CdCO}_3^0$  species dominates at pH values  $>8.2$ . Because pH values of surface and groundwaters found in the Coeur d'Alene River basin are typically lower than 8.2, the dominant aqueous cadmium species is expected to be  $\text{Cd}^{2+}$  with the  $\text{CdSO}_4^0$  species of secondary importance.

### ***Adsorption***

Cadmium adsorption, in contrast to other transition elements, often correlates with the cation exchange capacity of soil (Rai and Zachara 1986). This adsorption is impacted by concentrations of exchangeable cations such as Ca, Al, or Zn and becomes more significant at higher cadmium concentrations.

Peterson et al. (1983) and Serne et al. (1983) concluded that to accurately and quantitatively account for the migration of cadmium, one must take into consideration its pH dependent immobilization onto precipitated hydrous oxides. At low cadmium concentrations, specific adsorption onto metal oxyhydroxides via surface complexation (Dzombak 1986) appears to be important because of the sharp adsorption edges that result at lower concentrations. As mentioned previously, the exact shape of the adsorption edge will depend, among other things, on the concentrations of iron oxyhydroxides and cadmium in solution. At a cadmium concentration of approximately 56 µg/L and an iron concentration of 218 mg/L, cadmium adsorption onto iron oxyhydroxides goes from zero percent adsorbed to 100 percent adsorbed between pH values of approximately 5.0 and 7.5, respectively. Because lower iron concentrations are found in waters within the Coeur d'Alene River basin, the adsorption edge for cadmium will be shifted to the right which means that higher pH values must be reached for equivalent cadmium adsorption to occur.

The observed range of cadmium  $K_d$  values in the environment varies from 1.3 to 27 mL/g with a mean value of 6.7 mL/g. For the pH range of 5 to 9,  $K_d$  values varying from 3.0 mL/g to 567 mL/g were selected for use in modeling studies (Streng and Peterson 1989). In this study, different values were selected for different soil compositions.

Cation exchange on clay minerals is the probable cadmium adsorption mechanism at higher cadmium concentrations while specific adsorption onto metal oxides dominates at low cadmium concentrations. Adsorption coefficients ( $K_d$  values) for collocated water and soil samples in the Coeur d'Alene River basin are presented in Appendix G.3.

### ***Solid Species***

Cadmium minerals such as  $\text{CdSiO}_3$ ,  $\text{CdO}$  (monteponite),  $\text{Cd(OH)}_2$ ,  $\text{CdSO}_4 \cdot 2\text{H}_2\text{O}$ , and  $\text{Cd(OH)}_2$  are too soluble to form in soils (Lindsay 1979). Depending on the phosphate and carbonate concentrations,  $\text{CdCO}_3$  (otavite) or a cadmium phosphate such as  $\text{Cd}_3(\text{PO}_4)_2$  may precipitate from solution and control cadmium concentrations.

Under conditions sufficiently reducing to reduce sulfates to sulfides, cadmium sulfide ( $\text{CdS}$ ) precipitates and may function as a control on cadmium solubility.

In summary, at low cadmium and relatively high iron concentrations, specific adsorption onto iron oxyhydroxides may control the activity of cadmium. At relatively higher cadmium concentrations, ion exchange reactions may control cadmium solution concentrations in the Coeur d'Alene River basin.

## **IRON (Fe)**

### **Environmental Occurrence**

Typical native concentrations of iron in soil range from 7,000 to 550,000 mg/kg with an average concentration of 38,000 mg/kg (Lindsay 1979). Natural concentrations of iron in groundwaters range from 0.01 to 10 mg/L with extreme values exceeding 1,000 mg/L (Dragun 1988).

For the Coeur d'Alene River basin, the median and 90th percentile values for iron in uncontaminated soil studied by Gott and Cathrall (1980) were 36,000 mg/kg and 65,000 mg/kg, respectively. Gott and Cathrall (1980) also calculated the median (22,100 mg/kg) and 90th percentile (66,000 mg/kg) concentrations for iron in rock from throughout the Coeur d'Alene River basin.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved iron in the upper South Fork were 7.50 and 49.10 µg/L, respectively. In the Page-Galena mineral belt the respective concentrations were 12.00 and 26.33 µg/L. The corresponding values in the Pine Creek drainage were 12.92 and 25.86 µg/L. Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for dissolved iron was 12.00 µg/L and the 95th percentile value was 46.82 µg/L.

### **Environmental Chemistry**

The chemistry of iron in the Coeur d'Alene River basin is important for several reasons:

(1) Under reduced O<sub>2</sub> concentrations the Fe<sup>+2</sup>/Fe<sup>+3</sup> redox couple may determine, to a large extent, the redox status of the tailings leachates; (2) the iron oxides may act as adsorption surfaces (Jenne 1977; Means et al. 1978); (3) oxidation of pyrite (Fe<sub>2</sub>S) may cause acidification of the tailings solutions (Cherry et al. 1980); and (4) iron-bearing precipitates may decrease the permeability of soil materials and thus retard seepage away from tailings impoundments and mine adits (Gee et al. 1980; Langmuir and Riese 1981).

### ***Aqueous Species***

Species of Fe(II) and Fe(III) are stable under environmentally encountered aqueous pH and redox conditions. Under relatively oxidizing conditions, the  $\text{Fe}(\text{OH})^{2+}$  species is dominant between pH values of approximately 3.0 to 8.0, after which the  $\text{Fe}(\text{OH})_4^-$  species is dominant. Below a pH value of approximately 3.0, the  $\text{Fe}^{3+}$  species predominates in an oxidizing environment. In a reducing environment, the  $\text{Fe}^{2+}$  species dominates up to a pH value of 10, therefore, this species is expected to dominate under reducing conditions in the Coeur d'Alene River basin. In solutions with relatively high sulfate concentrations ( $10^{-3}$  M or 96 mg/L), the  $\text{FeSO}_4^0$  species is important or may dominate at even higher sulfate concentrations under a reducing environment. The  $\text{FeSO}_4^0$  species may dominate in waters where sulfate concentrations exceed 1,000 mg/L. However, sulfate concentrations this high are only expected to exist proximal to ores containing significant quantities of sulfates under oxidizing conditions. Typically, in the Coeur d'Alene River basin, it is anticipated that the dominant Fe(II) species will be  $\text{Fe}^{2+}$ . The  $\text{Fe}(\text{OH})^{2+}$  species will be dominant in the basin when iron is in the +3 oxidation state.

### ***Adsorption***

The oxides of iron are able to affect metal retention out of proportion to their total mass in soils and sediments because they can exist as coatings on these particles. Dzombak (1986) has made progress toward developing a uniform approach to the adsorption of metal ions onto amorphous iron. In his approach, the metals form complexes with the iron surface. It is expected that complexation of metals with iron oxyhydroxide surfaces will be an important mechanism for controlling aqueous metal concentrations in the Coeur d'Alene River basin. An iron oxyhydroxide surface complexation approach has been used previously to predict trace metal concentrations at mining sites (Peterson et al. 1986). Adsorption of metals onto iron oxyhydroxides was presented in Section 3.3.2.6.

### ***Solid Phases***

Iron chemistry is complex; the solubilities and crystallization sequence of various iron oxides are affected at times by such diverse factors as particle size and relative humidity (Murray 1979; Langmuir 1971), and reaction kinetics (Murray 1979; Langmuir 1969; Nordstrom et al. 1979). The solubility of Fe in soils is, in large measure, controlled by the low solubility of the oxides and hydroxides of Fe(III), with amorphous  $\text{Fe}(\text{OH})_3$  usually forming an upper limit on the activity of  $\text{Fe}^{+3}$ . The structure of  $\text{Fe}(\text{OH})_3$  (ferric hydroxide) ranges from the amorphous to the crystalline depending on the mode of formation and age.

Nordstrom et al. (1979) found that iron concentrations in acid mine waters appeared to be controlled by amorphous ferric hydroxide. Amorphous ferric hydroxide (ferrihydrite) also appeared to place an upper limit on iron concentrations in batch studies where uranium mill tailings solutions contacted clay materials for up to 16 months (Peterson and Krupka 1981). As discussed in detail elsewhere in this document, ion speciation/solubility calculations conducted on surface waters throughout the Coeur d'Alene River basin indicated that iron oxyhydroxide would be expected to precipitate.

The Na, K, and H jarosites (an iron bearing sulfate compound) were found to be oversaturated with respect to solution concentrations of acid mine waters (Peterson and Krupka 1981; Nordstrom et al. 1979). Jarosite was identified as having precipitated (by x-ray diffraction) in permeability columns (Peterson et al. 1982), but the rate of formation appears to be inhibited by some kinetic barrier.

Some iron solid phases potentially of importance in the Coeur d'Alene River basin are amorphous iron oxyhydroxides, iron sulfides, and, at low pH values, iron sulfates (e.g., jarosite). Iron sulfides and jarosites are expected to precipitate or function as solid-phase controls in or near ore bodies while ferric oxyhydroxides will precipitate in oxidizing environments such as surface waters.

## **ARSENIC (As)**

### **Environmental Occurrence**

Most arsenic found in air and water is in the parts per billion (ppb) concentration range while arsenic present in the earth's crust is found in concentrations of 2 to 5 parts per million (ppm) (Buhler 1972; Wagner 1972). Lindsay (1979) reports native soil concentrations slightly higher than these values with a range varying from 1.0 to 50 mg/kg and an average concentration of approximately 5.0 mg/kg. Normal arsenic concentrations in drinking water are in the <10 ppb range except in instances of high pollution (Braman 1975). Natural groundwater concentrations of arsenic are reported to vary from <1 –30 µg/L (Dragun 1988).

For the Coeur d'Alene River basin, the 90th percentile value for arsenic in soil examined by Gott and Cathrall (1980) was 22 mg/kg. Gott and Cathrall (1980) also calculated the 90th percentile (24 mg/kg) concentration for arsenic in rock from throughout the Coeur d'Alene River basin. Median values for arsenic were not reported in these studies.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved arsenic in the upper South Fork were 0.53 and 0.69  $\mu\text{g/L}$ , respectively. In the Page-Galena mineral belt the respective concentrations were 0.61 and 0.94  $\mu\text{g/L}$ . The corresponding values in the Pine Creek drainage were 0.20 and 0.51  $\mu\text{g/L}$ . Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for arsenic was 0.53 and the 95th percentile value was 0.91  $\mu\text{g/L}$ .

## **Environmental Chemistry**

### ***Aqueous Species***

Arsenic is stable in four oxidation states (-3, 0, +3, +5) under varying Eh and pH conditions, though metallic arsenic exists only rarely and the -3 oxidation state occurs only under extremely reducing conditions. The dominant oxidation states in natural aquatic systems are +3 and +5.

Arsenic removal from solution has been observed to be pH dependent. Gullledge and O'Connor (1973) attributed this pH dependency to the arsenic's changing speciation with changing pH. Frost and Griffin (1977) concluded that  $\text{H}_2\text{AsO}_4^-$  was the principal species adsorbed by clay minerals.

Hounslow (1980) noted that the rate of oxidation of arsenite to arsenate may be sluggish. Cherry et al. (1979) observed that the Fe(III) oxidation of As(III) to As(V) was barely discernible at high pH values but becomes appreciable at lower pH values.

Inorganic forms of arsenic are variably toxic depending on whether they are in the trivalent or pentavalent state. Arsenic in the reduced state [As(III)] is much more toxic, more soluble, and mobile than in the As(V) oxidation state. Hounslow (1980) states that arsenic in the reduced state is 60 times more toxic than arsenic in the oxidized state.

In groundwaters and surface waters of the Coeur d'Alene River basin, the  $\text{H}_2\text{AsO}_4^-$  species should be the dominant species in the pH range from approximately 3 to 7 and under conditions sufficiently oxidizing to maintain arsenic in the +5 oxidation state. In waters above a pH of approximately 7.0, the  $\text{HAsO}_4^{2-}$  species is expected to be predominant in waters of the Coeur d'Alene River basin. In conditions sufficiently reducing to maintain arsenic in the +3 oxidation state, the  $\text{H}_2\text{AsO}_3^-$  species will be the most important species. Under redox conditions capable of

reducing sulfate to sulfide, such as lake bed sediments in Coeur d'Alene Lake and the lateral lakes, the  $\text{AsS}^{2-}$  may dominate.

### ***Adsorption***

Akins and Lewis (1976) cite Jacobs et al. (1970) as saying that the arsenic concentrations in soils are directly proportional to the  $\text{Fe}_2\text{O}_3$  content of the soils. The removal of Fe and Al compounds from the soil either drastically reduced or completely eliminated arsenic adsorption. Akins and Lewis (1976) found that most of the arsenic in the soils studied was in the Fe-arsenate form with other forms such as Al- and Ca-arsenates predominating when the iron concentration was low. Water soluble arsenic was proportional to the total arsenic present in the soils and inversely proportional to the iron and aluminum present. Gulledge and O'Connor (1973) observed that ferric hydroxide  $[\text{Fe}(\text{OH})_3]$  was able to remove more arsenic(V) from solution than aluminum hydroxide. Hem (1977) stated that precipitation of ferric arsenate and coprecipitation with ferric hydroxide may be a major factor in As attenuation in geothermal waters.

Results from the work of Frost and Griffin (1977) indicated that As and Se would be more mobile in leachate passing through relatively pure clay materials under alkaline conditions.

Selective extraction data (Serne et al. 1983) demonstrated that hydrous iron oxides were contributing to the removal of arsenic in interactions between uranium mill tailings solutions and sediments. The extraction results indicated that amorphous iron oxide could be an important sink for arsenic with crystalline iron oxides and manganese oxides also contributing.

Streng and Peterson (1989) report arsenic  $K_d$  values ranging from 6.0 to 19 mL/g for the pH range of 5 to 9. Dragun (1988) provides  $K_d$  values for As(III) and As(V). The As(III)  $K_d$  values range from 1.0 to 8.3 with a mean of 3.3 while the As(V) values vary between 1.9 and 18 with a mean value of 6.7. Distribution coefficients computed from collocated water samples in the SFDR basin are presented in Section G-3.

### ***Solid Phases***

Wageman (1978) used the typical concentrations of arsenic in freshwater systems, along with the concentrations of 14 different metals found in these same systems to examine possible solid-phase controls on arsenic solubility. Four metals emerged from this study as possible candidates. The four were Ba, Cu, Fe and Cr. After these metals were examined more closely, it appeared that Ba, at concentrations found in ground waters, could be a possible solid phase control, with chromium and iron emerging as slightly less likely controls. Wageman (1978) goes on to say



that isomorphous substitution of arsenic for phosphate is found in such minerals as apatite  $[\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})]$ , libethenite  $[\text{Cu}_2(\text{OH})(\text{PO}_4)]$ , and in other complex arsenates analogously to the phosphates. The affinity of arsenic for iron may be due to the formation of such compounds. The existence of such an arsenic compound has not been identified but the analogous phosphate compound does exist as  $\text{FeH}_2\text{PO}_4(\text{OH})_2$  (Sillen and Martell 1964). Data in the literature are too sparse regarding barium and arsenic to come to any sort of conclusion as to the ability of a barium-arsenic solid to control the concentration of dissolved arsenic in solution.

In summary, the interaction of arsenic with iron is expected to exert a large influence on dissolved arsenic concentrations. This influence may result from complexation with iron surfaces or by the precipitation/coprecipitation of iron and arsenic.

## **MANGANESE (Mn)**

### **Environmental Occurrence**

Typical concentration ranges for manganese in soils range from 100 to 4,000 mg/kg while groundwater concentrations commonly range from <1 to 1,000 µg/L (Dragun 1988). Lindsay (1979) selected 600 mg/kg as the average manganese concentration in soils.

For the Coeur d'Alene River basin, the median and 90th percentile values for manganese in uncontaminated soil investigated by Gott and Cathrall (1980) were 1,333 mg/kg and 3,597 mg/kg, respectively. Gott and Cathrall (1980) also calculated the median (366 mg/kg) and 90th percentile (2,508 mg/kg) concentrations for manganese in rock from throughout the Coeur d'Alene River basin.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved manganese in the upper South Fork were 1.50 and 22.17 µg/L, respectively. In the Page-Galena mineral belt the respective concentrations were 2.07 and 4.00 µg/L. The corresponding values in the Pine Creek drainage were 1.33 and 2.35 µg/L. Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for dissolved manganese was 1.50 and the 95th percentile value was 21.22 µg/L.

## **Environmental Chemistry**

### ***Aqueous Species***

Manganese can exist in three distinct valence states (+2, +3, and +4), however, the +3 valence state may disproportionate and form ions of the +2 and +4 valence states. The +2 oxidation state is expected to be the predominant valence state under conditions anticipated in the Coeur d'Alene River basin. In the absence of high concentrations of anions, the  $\text{Mn}^{2+}$  species should predominate up to a pH of approximately 10, after which the  $\text{Mn}_2(\text{OH})^{3+}$  species predominates (Baes and Mesmer 1976). At high solution concentrations of either bicarbonate or sulfate, the  $\text{MnHCO}_3^+$  species or  $\text{MnSO}_4$  neutral ion pair may become important.

### ***Adsorption***

Specific adsorption of manganese on iron oxides occurs but the strength of adsorption is weak. Regression analyses indicate that at high solution concentrations of manganese, cation exchange may be an important mechanism for manganese retention by soils. After a review of the literature, Streng and Peterson (1989) selected manganese distribution coefficients ( $K_d$ s) that varied between 17 and 37 (pH range of 5 to 9) depending upon the soil matrix. Dragun (1988) listed manganese  $K_d$  values varying from 0.2 to 10,000 with a mean\* value of 148. Positive correlations between manganese and iron and between manganese and other metals in the Coeur d'Alene River basin are discussed in Appendix G.3.

### ***Solid Phases***

Jenne et al. (1980) suggest that  $\text{MnHPO}_4$  could be a possible manganese control in a variety of environments. Although  $\text{MnHPO}_4$  has been discussed in the literature (Lindsay 1979), a cursory review of x-ray and mineralogical references has produced no evidence for the existence of this solid in natural systems. Rhodochrosite ( $\text{MnCO}_3$ ) has been shown to readily precipitate from solution (Johnson 1982). Peterson et al. (1986) postulated that rhodochrosite was precipitating and dissolving as the pH changed and controlling manganese concentrations in uranium mill tailings solutions. Based on the circumneutral pH values of many waters in the Coeur d'Alene River basin, rhodochrosite could precipitate/dissolve and control manganese concentrations in these waters.

## **MERCURY (Hg)**

### **Environmental Occurrence**

Naturally occurring soil concentrations of mercury are low, ranging from 0.01 to 0.08 mg/kg. Lindsay (1979) reports that the average mercury concentrations in soils are approximately 0.03 mg/kg. Natural concentrations of this element in groundwater are also low (<1.0 µg/L, Dragun 1988).

For the Coeur d'Alene River basin, the median and 90th percentile values for mercury in uncontaminated soil examined by Gott and Cathrall (1980) were 0.1 mg/kg and 0.3 mg/kg, respectively. Gott and Cathrall (1980) also calculated the median (0.03 mg/kg) and 90th percentile (0.17 mg/kg) concentrations for mercury in rock from throughout the Coeur d'Alene River basin.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved mercury in the upper South Fork were 0.10 and 0.10 µ/L, respectively. In the Page-Galena mineral belt the respective concentrations were 0.10 and 0.73 µ/L. The corresponding values in the Pine Creek drainage were 0.10 and 0.10 µ/L. Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for dissolved mercury was 0.10 and the 95th percentile value was 0.66 µ/L.

### **Environmental Chemistry**

#### ***Aqueous Species***

In aqueous solutions, mercury exists in the 0, +1, and +2 oxidation states. Mercury also presents itself in methylated forms with the CH<sub>3</sub>HgOH species being the dominate methylmercury form in the environment. For mercury(II), in the absence of organic matter and anions that do not result from the dissociation of water, the Hg<sup>2+</sup> species is dominant up to a pH of approximately 2 with the HgOH<sup>+</sup> species dominant between pH values of approximately 2 and 4. Above a pH of 4, the Hg(OH)<sub>2</sub><sup>0</sup> species predominates. Mercury forms strong complexes with organic matter and chloride. Accordingly, a large portion of the mercury in solution may be complexed with organic matter and chloride if they are present. Mercury(II) complexes with organic matter may comprise >99.9% of the mercury in fresh waters (Mantoura et al. 1978). The aqueous species of

mercury expected to dominate in surface and groundwaters of the Coeur d'Alene River basin is  $\text{Hg}(\text{OH})_2^0$ .

### ***Adsorption***

Upon reviewing the literature, Streng and Peterson (1989) selected conservative (i.e., low) distribution coefficients ( $K_d$ s) for mercury ranging from 322 to 5,280 mL/g in the pH range of 5 to 9. Under given conditions ( $1.0 \times 10^{-3}$  mol Fe,  $1.0 \times 10^{-6}$  mol Hg, and  $4.0 \times 10^{-5}$  mol  $\text{Cl}^-$ ) mercury adsorption on amorphous ferric oxyhydroxide will go from 0 to 100 percent adsorbed between a pH of approximately 3 and 5, respectively (Dzombak 1986).

### ***Solid Phases***

Mercury is considered a chalcophilic element in that it tends to concentrate in sulfides such as encountered throughout the Coeur d'Alene River basin. Cinnabar (alpha  $\text{HgS}$ ) and metacinnabar (beta  $\text{HgS}$ ) occur naturally in the uncombined state with smaller quantities of mercury found in other sulfides (Bodek et al. 1988).

## **COPPER (Cu)**

### **Environmental Occurrence**

Indigenous soil concentrations of copper reportedly (Dragun 1988) range from 2 to 100 mg/kg with an average value of 30 mg/kg (Lindsay 1979). Dragun (1988) also states that naturally occurring copper concentrations in groundwater range from <1 to 30  $\mu\text{g/L}$ .

For the Coeur d'Alene River basin, the median and 90th percentile values for copper in uncontaminated soil studied by Gott and Cathrall (1980) were 28 mg/kg and 53 mg/kg, respectively. Gott and Cathrall (1980) also calculated the median (12 mg/kg) and 90th percentile (69 mg/kg) concentrations for mercury in rock from throughout the Coeur d'Alene River basin.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved copper in the upper South Fork were 0.63 and 1.50  $\mu\text{g/L}$ , respectively. In the Page-Galena mineral belt the respective concentrations were 0.88 and 1.28  $\mu\text{g/L}$ . The corresponding values in

the Pine Creek drainage were 0.43 and 0.84  $\mu\text{g/L}$ . Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for dissolved copper was 0.63 and the 95th percentile value was 1.48  $\mu\text{g/L}$ .

## **Environmental Chemistry**

### ***Aqueous Species***

In aqueous solutions, copper exists in the +1 oxidation state under reducing conditions and the +2 oxidation or valence state under oxidizing conditions. Under reducing conditions in equilibrium with atmospheric  $\text{CO}_2$ , the  $\text{Cu}^+$  species predominates between a pH of approximately 4 and 10 and is expected to be the dominant species in the Coeur d'Alene River basin. Below this pH range (4 to 10), the  $\text{Cu}^{2+}$  species predominates and above this range the  $\text{Cu}(\text{CO}_3)_2^{2-}$  species is dominant. Under oxidizing conditions found in surface waters of the Coeur d'Alene River basin and in equilibrium with atmospheric  $\text{CO}_2$ , the  $\text{Cu}^{2+}$  species is expected to be dominant up to a pH value of approximately 7. Between the pH range of 7 and 10, the  $\text{Cu}(\text{OH})_2^0$  species should predominate in the Coeur d'Alene River basin.

### ***Adsorption***

Dragun (1988) lists a range of  $K_d$  values for copper (1.4 to 333) with a mean\*  $K_d$  value of approximately 22. In selecting conservative  $K_d$  values to use in estimating mobility, values ranging from 42 to 336 (pH range of 5 to 9) were chosen (Streng and Peterson 1989).

### ***Solid Phases***

Based on thermodynamic solubility calculations (Lindsay 1979), soil-Cu and cupric ferrite ( $\text{CuFe}_2\text{O}_4$ ) were very stable under oxidizing conditions, while cuprous ferrite ( $\text{Cu}_2\text{Fe}_2\text{O}_4$ ) was the stable phase under reducing conditions. Adsorption studies have indicated that solid phases control solution concentrations of copper with  $\text{Cu}(\text{OH})_2$  being among the various solid phases implicated. Chalcopyrite ( $\text{CuFeS}_2$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ) are ores commonly found in the Coeur d'Alene River basin. Copper also substitutes for metals in other ore types in the Coeur d'Alene River basin such as tetrahedrite  $[(\text{Cu}, \text{Fe}, \text{Zn}, \text{Ag})_{12}\text{Sb}_4\text{S}_{13}]$ .

## **SILVER (Ag)**

### **Environmental Occurrence**

Soil concentrations of silver occurring naturally range from 0.01 to 5.0 mg/kg. Lindsay (1979) selects 0.05 mg/kg as the average silver concentration in soils. Natural concentrations of this element in groundwater are typically <5.0 µg/L (Dragun 1988).

For the Coeur d'Alene River basin, the median and 90th percentile values for silver in uncontaminated soil investigated by Gott and Cathrall (1980) were 0.6 mg/kg and 1.1 mg/kg, respectively. Gott and Cathrall (1980) also calculated the median (0.2 mg/kg) and 90th percentile (1 mg/kg) concentrations for silver in rock from throughout the Coeur d'Alene River basin.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved silver in the upper South Fork were 0.06 and 0.14 µg/L, respectively. In the Page-Galena mineral belt the respective concentrations were 0.06 and 0.08 µg/L. The corresponding values in the Pine Creek drainage were 0.04 and 0.08 µg/L. Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for dissolved silver was 0.06 and the 95th percentile value was 0.14 µg/L.

### **Environmental Chemistry**

#### ***Aqueous Species***

The +2 (AgII) and +3 (AgIII) oxidation states of silver are known to exist but are unstable under the normal range of environmental conditions. The dominant aqueous species anticipated to be encountered in the Coeur d'Alene River basin is  $\text{Ag}^+$  with the  $\text{AgOH}^0$  neutral aqueous pair of secondary importance. Silver forms strong complexes with sulfide and sulfate. Under reducing conditions and a concentration of 0.01 M sulfate,  $10^{-5}$  M sulfide, and 0.6 M chloride, the  $\text{AgSH}^0$  species will dominate over a wide range of pH values. Under these same conditions, the  $\text{AgCl}_2^-$  and  $\text{AgCl}^0$  species will be present to a greater extent than the  $\text{Ag}^+$  species (Bodek et al. 1988).

### ***Adsorption***

Typical  $K_d$  values for silver range from 10 to 1,000 mL/g with a mean value\* of 110 (Dragun 1988). For the pH range of 5 to 9, Streng and Peterson (1989) report conservative  $K_d$  values for silver ranging from 0.4 to 40 depending upon the specific soil matrix.

### ***Solid Phases***

Because of the relatively high solubility of oxides, sulfates, carbonates, and phosphates of silver, these compounds are not expected to precipitate from solution and control the dissolved silver concentrations. Under reducing conditions and in the presence of sulfur, silver sulfide ( $\text{Ag}_2\text{S}$ ) is expected to form. Silver metal [ $\text{Ag}_0$ ] may also form under reducing conditions. In the presence of sufficient concentrations of halides, the  $\text{AgCl}$  and  $\text{AgBr}$  solids may form but are not expected to form in the Coeur d'Alene River basin. As mentioned, the Coeur d'Alene mining district has become the largest silver producer in the world. Almost all this silver is mined from tetrahedrite [ $(\text{Cu}, \text{Fe}, \text{Zn}, \text{Ag})_{12}\text{Sb}_4\text{S}_{13}$ ] and silver-rich galena ( $\text{PbS}$ ) or may exist in other ores that are mixed with the galena. Other silver-containing solid phases (ores) found in the Coeur d'Alene River basin include argentite ( $\text{Ag}_2\text{S}$ ) and pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ).

## **ANTIMONY (Sb)**

### **Environmental Occurrence**

Naturally occurring soil concentrations of antimony vary from 0.6 to 10 mg/kg (Dragun 1988).

For the Coeur d'Alene River basin, the median and 90th percentile values for antimony in uncontaminated soil studied by Gott and Cathrall (1980) were 1.1 mg/kg and 5.8 mg/kg, respectively. Gott and Cathrall (1980) also calculated the median (1 mg/kg) and 90th percentile (7.9 mg/kg) concentrations for antimony in rock from throughout the Coeur d'Alene River basin.

In the draft report listing background concentrations in surface waterways of the Coeur d'Alene River basin, (URS and CH2M HILL 2000), similarities in ore types were used to divide the Coeur d'Alene River basin into three regions for determination of the baseline surface water concentrations. Based on this assessment, the median and 95th percentile values for dissolved silver in the upper South Fork were 0.25 and 0.27  $\mu\text{g/L}$ , respectively. In the Page-Galena mineral belt the respective concentrations were 0.50 and 3.19  $\mu\text{g/L}$ . The corresponding values in the Pine

Creek drainage were 0.21 and 0.48  $\mu\text{g/L}$ . Collectively, for surface waters in the entire South Fork basin, the median baseline concentration for dissolved antimony was 0.25 and the 95th percentile value was 2.92  $\mu\text{g/L}$ .

## **Environmental Chemistry**

### ***Aqueous Species***

Antimony exhibits various valence states (-3, 0, +3, and +5) but only the +3 and +5 states are important in aqueous solutions. The +3 oxidation state of antimony tends to prevail under reducing conditions and the +5 oxidation state under oxidizing conditions. The dominant Sb(VI) species up to a pH value of approximately 2.8 is  $\text{Sb}(\text{OH})_5^\circ$  after which the  $\text{Sb}(\text{OH})_6^-$  species is dominant. In relatively reducing environments, the  $\text{Sb}(\text{OH})_3^\circ$  species is dominant between pH values of 1.5 and 11.2. Above a pH value of 11.2, the  $\text{Sb}(\text{OH})_4^-$  species predominates (Rai and Zachara 1986). Accordingly, in the Coeur d'Alene River basin, the  $\text{Sb}(\text{OH})_6^-$  species is expected to be the major species under oxidizing conditions and the  $\text{Sb}(\text{OH})_3^\circ$  species under relatively reducing conditions.

### ***Adsorption***

In a circumneutral (5 to 9) pH range such as is commonly encountered in the Coeur d'Alene River basin, selected distribution coefficients ( $K_d$ ) for antimony ranged from 2 to 16 (Streng and Peterson 1989). These are conservative values, based on a review of the literature, suggested for use in transport modeling exercises.

### ***Solid Phases***

The principal ores of antimony in the Coeur d'Alene River basin are tetrahedrite  $[(\text{Cu}, \text{Fe}, \text{Zn}, \text{Ag})_{12}\text{Sb}_4\text{S}_{13}]$  and stibnite ( $\text{Sb}_2\text{S}_3$ ). Other ores that are found below the zone of oxidation include polybasite  $[(\text{Ag}, \text{Cu})_{10}\text{Sb}_2\text{S}_{11}]$ , pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ), bournonite ( $\text{PbCuSbS}_3$ ), meneghinite ( $\text{Pb}_3\text{Sb}_7\text{S}_{23}$ ), boulangerite ( $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ ), and jamesonite ( $\text{PbFeSb}_6\text{S}_{14}$ ).

Once the ores are exposed to air and oxidation occurs, only very soluble solid phases of antimony are known to exist. Consequently, precipitation/dissolution of antimony solid phases is not expected to control aqueous antimony concentrations in the Coeur d'Alene River basin. Concentrations of antimony are expected to be controlled by adsorption/desorption reactions rather than precipitation/dissolution reactions.



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### **G.3**

#### **ESTIMATION OF DISTRIBUTION COEFFICIENTS ( $K_d$ ) FOR LEAD, ZINC, AND CADMIUM IN THE COEUR D'ALENE RIVER BASIN**

### **G.3, ESTIMATION OF DISTRIBUTION COEFFICIENTS ( $K_d$ ) FOR LEAD, ZINC, AND CADMIUM IN THE COEUR D'ALENE RIVER BASIN**

#### **LEAD**

The EPA (USEPA 1999a, 1999b) conducted a review of geochemistry and available distribution coefficients ( $K_d$  values) for lead. Data from a number of authors were reviewed, however, only data from Gerritse et al. (1982) and Rhoades et al. (1992) were used to develop regression coefficients. The following polynomial relationship (equation 1) with a coefficient of determination ( $r^2$ ) of 0.971 existed between  $K_d$  and soil pH measurements.

$$K_d \text{ (ml/g)} = 1639 - 902.4(\text{pH}) + 150.4(\text{pH})^2 \quad \text{Eq. 1}$$

A relationship between lead concentrations and  $K_d$  values was developed at a fixed pH using data for Hanford soils (equation 2).

$$K_d \text{ (ml/g)} = 9,550 C^{-0.335} \quad \text{Eq. 2}$$

where C is the equilibrium concentration of lead in  $\mu\text{g/L}$ . Using Equations 1 and 2, the following lookup table was generated (Table G.3-1).

In Table G.3-1, the highest  $K_d$  values occur at the lowest concentrations and highest pH values while the lowest  $K_d$  values are found at the highest concentrations and the lowest pH values. Table G.3-1 does not account for the well-established variation of  $K_d$  with soil type and should be used with caution. The pH relationship was developed from data on Hanford soils, which tend to have a large sand-sized component.

The values in Table G.3-1 are in general agreement with values reported by Dragun (1988) and Streng and Peterson (1989). Dragun reported  $K_d$  values ranging from 4.5 to 7,640 mL/g with a mean (geometric mean) value of approximately 100. For the pH range of 5 to 9, Streng and Peterson (1989) selected conservative (i.e., low) values to use in modeling studies of 234 to 1830 mL/g, depending on the soil composition.

For surface waters in the South Fork basin, the dissolved lead concentrations are typically less than 10  $\mu\text{g/L}$  and the pH will generally fall in the range of 6.4 to 8.7. Based on Table G.3-1,  $K_d$  values applicable to basin surface waters are expected to fall in the range of 1,950 to 23,270 mL/g.

Collocated samples from throughout the Coeur d'Alene River basin were identified to obtain in situ  $K_d$  values. The samples identified were collected in December 1998 (URS 2000) coincident with the installation of monitoring wells. Sediment samples were collected at varying depths during well installation. The wells were completed with sand packs to within approximately 5 feet of the surface. Water samples were then collected from various depths. These water-sampling depths most often were located at depths similar to depths from which sediment samples were collected.

Water sample depths with dissolved concentrations of lead, zinc, and cadmium were first matched to soil sample depths. The total concentrations of sediment samples reported in mg/kg were paired with the corresponding dissolved concentrations of the metals. All samples collected at depths greater than 20 feet were then removed from the database along with one anomalous sample. The  $K_d$  values computed from the anomalous sample were orders of magnitude larger than typical values for each of the metals (lead, zinc, and cadmium) and distorted the sample mean. The  $K_d$  values computed from dissolved and sediment concentrations for this sample ranged from greater than 1 million for zinc to greater than 105 million for lead. All samples with dissolved lead concentrations of 1.0  $\mu\text{g/L}$  or less were excluded from the analysis. These samples were excluded because many of the concentrations were less than the instrument detection limits and, based on professional judgement,  $K_d$  values computed from such samples were unrepresentative.

The computed in situ  $K_d$  values ( $n = 28$ ) were then averaged. The average in situ  $K_d$  value computed for lead was 28,572 mL/g. Computed  $K_d$  values ranged from a low of 4 to a high (excluding the so called "anomalous" sample) of 415,254 mL/g. The median  $K_d$  value was 14,055 mL/g. If the samples with dissolved lead concentrations less than or equal to 1  $\mu\text{g/L}$  are included ( $n = 45$ ), the average lead  $K_d$  value was 186,000 with a median of 20,700. These data are summarized in Table G.3-2.

When including samples with aqueous lead concentrations less than 1  $\mu\text{g/L}$ , the average  $K_d$  value increased from 28,572 mL/g to 186,000. As noted previously, inclusion of low concentrations, some of which were at or below the instrumental detection limits, often resulted in abnormally high  $K_d$  values. The median values computed for the two sample sizes ( $n = 28$  and  $n = 45$ ) were closer to one another and close to the range of values reported in the literature (see preceding paragraphs). In lieu of site-specific experimental data, a reasonable  $K_d$  value for the basin appears to be 14,000 mL/g. This value is in general agreement with the values reported by the EPA (USEPA 1999b), Strenge and Peterson (1989), and Dragun (1988).



## ZINC

In their review of  $K_d$  values, the EPA (USEPA 1999a, 1999b) did not review available  $K_d$  values for zinc. There is a wide range of zinc  $K_d$  values reported in the literature. The values reported by Dragun (1988) ranged from 0.1 to 8,000 mL/g with a mean of 16.4. For the pH range of most interest in the Coeur d'Alene River basin (5 to 9), Streng and Peterson (1980) selected conservative (i.e., low)  $K_d$  values for modeling ranging from 13.0 to 1,460 mL/g.

Lindsay (1979) has attributed the solubility of zinc in soils to a soil-Zn adsorption equilibrium and has, moreover, developed an expression (equation 3) to predict zinc concentrations in soils.

$$\log [\text{Zn}^{2+}] = 5.8 - 2\text{pH} \quad \text{Eq. 3}$$

where  $[\text{Zn}^{2+}]$  is expressed in moles/L.

Based on this relationship, at a neutral pH value (7.0), the concentration of  $\text{Zn}^{2+}$  in solution would be approximately 0.41  $\mu\text{g/L}$ . Correspondingly, the expected zinc concentration at a pH of 6.0 would be approximately 41  $\mu\text{g/L}$ . These concentrations are below values found in groundwaters of the Coeur d'Alene River basin; therefore, soil-Zn adsorption is not expected to control solution concentrations of zinc.

The same collocated samples (discussed under lead section) were used to obtain in situ  $K_d$  values for zinc (URS 2000). As with lead, analyses of sediment samples reported in mg zinc/kg were paired with the corresponding dissolved concentrations of zinc. All samples collected at depths greater than 20 feet were then removed from the database along with the one anomalous sample.

The computed in situ  $K_d$  values ( $n = 45$ ) were then averaged. The mean in situ  $K_d$  value computed for zinc was 954 mL/g. Computed  $K_d$  values ranged from a low of 1 mg/kg to a high (excluding the so called "anomalous" sample) of 21,009 mL/g. The median in situ  $K_d$  value for zinc was 53 mL/g. Table G.3-3 summarizes these data.

Again, the median value appears to provide a more realistic estimate of the  $K_d$  value for zinc because a few large values tend to have a pronounced impact on the mean. In lieu of site-specific experimental data, a reasonable zinc  $K_d$  value for the basin appears to be 53 mL/g. This value is in general agreement with the values reported by Streng and Peterson (1989), and Dragun (1988).

## CADMIUM

The EPA (USEPA 1999a, 1999b) conducted a review of geochemistry and available  $K_d$  values for cadmium. A total of 174 cadmium  $K_d$  values were found in the literature. Regression analyses were performed to determine the relationships between  $K_d$  values and assorted parameters such as clay content, cation exchange capacity, total organic carbon, pH, and iron oxides. The most significant correlation ( $r = 0.75$ ) occurred between pH and the  $\log K_d$ . The correlation between pH and the  $\log K_d$  was significant at the 0.001 level of probability.

The following relationship existed between cadmium  $K_d$  values and soil pH measurements.

$$\text{Log } K_d (\text{mL/g}) = -0.54 + 0.45 (\text{pH}) \quad \text{Eq. 4}$$

Equation 4 was used to develop the following lookup table (Table G.3-4). Cadmium  $K_d$  values varied by 2 orders of magnitude at any pH. The  $K_d$  ranges in Table G.3-4 are large because the data scatter around the regression line was used to estimate minimum and maximum pH values.

In Table G.3-4, higher  $K_d$  values occur at higher pH values. Table G.3-4 does not account for the variation of  $K_d$  with soil type because the correlation coefficient between  $K_d$  and clay content was nonsignificant at the 5 percent level of probability. The wide range of values somewhat limits their usefulness.

The values in Table G.3-4 are in general agreement with values reported by Streng and Peterson (1989). For the pH range of 5 to 9,  $K_d$  values varying from 3.0 to 567 were selected for use in modeling studies. In this study (Streng and Peterson), different values were selected for different soil compositions. Dragun (1988) reported that the observed range of cadmium  $K_d$  values varied from 1.3 to 27 with a mean of 6.7.

For surface waters and groundwaters in the South Fork basin, pH values generally fall in the range of 5 to 8. Based on Table G.3-4,  $K_d$  values applicable to these waters are expected to fall in the range of 8 to 4,000 mL/g. The regression equation (equation 4) predicts a  $K_d$  value of 407 at a pH of 7.0.

The collocated samples (discussed under lead section) collected in December 1998 were used to obtain in situ  $K_d$  values for cadmium (URS 2000). As with lead and zinc, analyses of sediment samples reported in mg cadmium/kg were paired with the corresponding dissolved concentrations of cadmium. All samples collected at depths greater than 20 feet were then removed from the database along with the one anomalous sample.

The computed in situ  $K_d$  values ( $n = 45$ ) were then averaged. The mean in situ  $K_d$  value computed for cadmium was 640 mL/g. Computed  $K_d$  values ranged from a low of 1 mL/g to a high (excluding the so called “anomalous” sample) of 11,333 mL/g. The median in situ  $K_d$  value for cadmium was 59 mL/g. Table G.3-5 summarizes these data.

As with lead and zinc, the median value appears to provide a more realistic estimate of the  $K_d$  value for cadmium because a few large values tend to have a pronounced impact on the mean. In lieu of site-specific experimental data, a reasonable cadmium  $K_d$  value for the basin appears to be 59 mL/g. This value is in general agreement with the values reported by EPA (USEPA 1999b), Streng and Peterson (1989), and Dragun (1988).

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**Table G.3-1**  
**Relationship Between Lead Concentrations, Soil pH, and  $K_d$  Values**

Equilibrium Lead Concentration ( $\mu\text{g/L}$ )	$K_d$ (mL/g)	Soil pH		
		4.0 – 6.3	6.4 – 8.7	8.8 – 11.0
0.1 – 0.9	Minimum	940	4,360	11,520
	Maximum	8,650	23,270	44,580
1.0 – 9.9	Minimum	420	1,950	5,160
	Maximum	4,000	10,760	20,620
10 – 99.9	Minimum	190	900	2,380
	Maximum	1,850	4,970	9,530
100 – 200	Minimum	150	710	1,880
	Maximum	860	2,300	4,410

Source: U.S. EPA 1999b

**Table G.3-2**  
**Distribution Coefficients ( $K_d$  values) for Lead (mL/g) Computed from Collocated Water and Soil Samples From Throughout the Coeur d'Alene Basin (n = 28 and 45)**

Distribution Coefficients, $K_d$ values, Expressed in mL/g					
number = 28				n = 45	
Average	Low	High	Median	Average	Median
28,572	4	415,254	14,055	186,000	20,700

**Table G.3-3**  
**Distribution Coefficients ( $K_d$  values) for Zinc Computed From Collocated Water and Soil Samples From Throughout the Coeur d'Alene Basin (n = 45)**

Distribution Coefficients, $K_d$ values, Expressed in mL/g			
number = 45			
Mean	Low	High	Median
954	1	21,009	53

**Table G.3-4**  
**Relationship Between pH and  $K_d$  Values**

$K_d$ (mL/g)	Soil pH		
	3 – 5	5 – 8	8 – 10
Minimum	1	8	50
Maximum	130	4,000	12,600

**Table G.3-5**  
**Distribution Coefficients ( $K_d$  values) for Cadmium Computed from Collocated Water and Soil Samples from Throughout the Coeur d'Alene Basin (n = 45)**

Distribution Coefficients, $K_d$ values, Expressed in ml/g			
number = 45			
Mean	Low	High	Median
640	1	11,333	59

#### **G.4**

### **LEACHING AND CATION EXCHANGE CAPACITY STUDIES IN THE COEUR D'ALENE RIVER BASIN**

#### **G.4, LEACHING AND CATION EXCHANGE CAPACITY STUDIES IN THE COEUR D'ALENE RIVER BASIN**

Toukan (1971) collected four core samples from a tailings pond at Canyon Creek. The cation exchange capacities (CECs) of the samples were calculated using different metals under various pH regimes (pH values of 4, 5, 6, 7, 8, 9, and 10) and metal concentrations. Cation exchange capacities of the tailings did not increase or decrease linearly. Although there were some exceptions, generally, the highest CEC was measured at the highest pH value (pH of 10) while the lowest CEC was observed at a pH value of 6.

Except for the CECs calculated using lead, the CECs of the tailings were typically low compared to CECs encountered in soils. In mineral soils, a typical CEC may vary from several milliequivalents (meq) per 100 grams (g) soil to 50 or 60 meq/100 g. The CECs of soils rich in organic matter may exceed 200 meq/100 g. When cations such as calcium, sodium, cadmium, zinc, and copper were used to determine the CEC of the tailings, the CECs of the tailings were always between 1 and 10 meq/100 g. However, when lead was used as the cation to evaluate the CEC of the tailings, the CEC was usually between approximately 200 and 400 meq/100 g. Lead may have been precipitating in these solutions as the concentration was approximately 1 normal. Precipitation of lead would explain the values obtained when lead was used to compute the CEC.

In the various experiments, lead always had the greatest selectivity for the exchange sites. The selectivity order of the other cations for exchange sites varied from test to test. In general, however, calcium and magnesium usually had a greater selectivity (preference) for exchange sites than zinc, cadmium, or copper. Zinc typically had a greater selectivity than cadmium or copper. Because of the low CEC, the majority of metals associated with tailings should be associated with the mineralogic structure of the tailings and not with the solid surfaces.

Galbraith and Williams (1972), in a study of metal leaching from old mine tailings, treated the Cataldo Mission Flats as a large tailings pile. In an initial sampling episode, they collected samples from the 3- and 6-foot depths. Subsequently, Galbraith and Williams (1972) collected samples every 6 inches in 3 additional holes augured to several feet below the water table. Groundwater samples were also collected from the holes. Laboratory experiments were conducted to support initial conclusions reached in an analysis of field samples.

Concentrations of metals in solutions obtained from batch leaching experiments were significantly lower than metal concentrations observed in tailings pore waters below the water table. For example, lead and zinc concentrations leached in batch experiments averaged 0.2 and



0.6 mg/L, respectively, while lead (0.8 mg/L) and zinc (52 mg/L) concentrations found in tailings pore waters were higher by 4 to 8 fold. The lower concentrations noted in laboratory experiments were attributed to slower weathering processes and the delayed action of microbial organisms (Galbraith and Williams 1972).

La Force et al. (1998) collected moist cores from the riverbank of the South Fork and main stem Coeur d'Alene River at three locations. These samples were subjected to selective chemical extractions and flooding simulations conducted in laboratory columns. Only manganese, lead, and zinc were detected in the exchangeable fraction while the remainder of the metals were below detection limits. Zinc concentrations in the exchangeable fraction were particularly high (303 to 13,400 mg zinc/kg sediment). These same elements (manganese, lead, and zinc) were also the predominant elements found in the carbonate fraction though some elements may have dissolved from the iron fraction during the carbonate extraction. The highest concentrations of arsenic were associated with the iron fraction while iron, lead, and manganese were the predominant elements found in the organic fraction of the sediments.

In column studies to mimic flooding events, sediment cores were subjected to simulated high-flow events (with oxygen purged) and low-flow events (oxygen present) with and without nutrient addition. Nutrients were added in the form of glucose and ammonium sulfate. Columns with nutrient addition consistently released higher metal concentrations than columns without nutrient addition (Table G.4-1).

In general, for the three locations (only two locations are presented in Table G.4-1), metal concentrations increased 5-fold to 100-fold over unamended solutions. Nutrient additions increased metal concentrations regardless of whether the solution was purged of oxygen (with N<sub>2</sub>) or contained oxygen. Microbial growth in the amended solutions was thought to account for the observed reduction in redox potential. As a consequence of the lowered redox potential, iron and manganese were reduced and dissolved, releasing adsorbed metal ions into solution.

There are implications for the feasibility study in these laboratory studies. Leaching studies conducted as part of the feasibility study should take into account the slower weathering processes and the delayed action exhibited by microbial organisms in laboratory columns compared to tailings encountered in the field. The experiments with nutrient additions illustrate the enhanced leaching impact of nutrients and suggest measures should be undertaken to limit nutrient addition (e.g., septic-tank sewage) to the aqueous system as a means of reducing dissolved metal concentrations.

## REFERENCES

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- LaForce, M.J., S.E. Fendorf, G.C. Li, G.M. Scheider, and R.F. Rosenzweig. 1998. "Heavy Metals in the Environment: A Laboratory Evaluation of Trace Element Mobility from Flooding and Nutrient Loading of Coeur d'Alene River Sediments." *J. Environ. Qual.* 27:318-328.
- Toukan, Z.R. 1971. Cation Exchange Properties of Mine Tailings. A thesis presented in partial fulfillment of the requirement for the Degree of Master of Science in Geological Engineering, University of Idaho Graduate School.

**Table G.4-1**  
**Comparison of Columns With No Nutrient Addition to Columns**  
**with Nutrient Addition at Two Locations on the South Fork**  
**and Main Stem Coeur d'Alene River**

Location	Stimulated High-Flow Event	
	No Addition (µg/L)	Nutrient Addition (µg/L)
<b>Main Stem Coeur d'Alene River</b>		
Lead	70	7,570
Zinc	180	8,540
Arsenic	40	1,540
<b>Cataldo</b>		
Lead	2,240	3,340
Zinc	6,700	8,080
Arsenic	10	450

## **G.5**

### **GEOCHEMICAL REACTIONS AND PROCESSES AFFECTING METAL FATE AND TRANSPORT**

## **G.5, GEOCHEMICAL REACTIONS AND PROCESSES AFFECTING METAL FATE AND TRANSPORT**

Metal fate and transport in the Coeur d'Alene River basin is affected by numerous geochemical processes. The primary processes operating on the source of the metals (e.g., geologic formations and mine wastes) and causing their mobilization and transport through surface water, groundwater, and sediment are presented in this section.

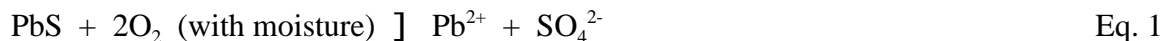
### **ACID- AND BASE-GENERATING PROCESSES**

Sulfide minerals, particularly iron pyrite ( $\text{FeS}_2$ ), have the potential to produce low-pH waters. Nordstrom et al. (2000) measured negative pH values (-3.6) underground in the Richmond Mine at Iron Mountain, CA). Waters emanating from the Kellogg Tunnel at the Bunker Hill complex can exhibit pH values below 3.0. However, the majority of waters in the Coeur d'Alene River basin have near neutral pH values or are only slightly acidic. The importance of different types of deposits and their effects on pH in surface water in the basin are presented in this section.

#### **Specific Acid- and Base-Generating Minerals**

The principal acid-generating mineral in the basin is pyrite ( $\text{FeS}_2$ ). The main base-generating mineral in the basin is calcite ( $\text{CaCO}_3$ ). Equations to illustrate the acid- or base-generating capabilities of pyrite and calcite are found below.

The principal ore mineral in the northern and eastern portion of the basin is galena ( $\text{PbS}$ ). Galena is not an acid-forming mineral as indicated by Equation 1. Analogous reactions could be written and conclusions derived for sphalerite ( $\text{ZnS}$ ) and greenockite ( $\text{CdS}$ ).



If the formation processes occur more rapidly than the removal processes, the  $\text{Pb}^{2+}$  and  $\text{SO}_4^{2-}$  ions may combine to form anglesite ( $\text{PbSO}_4$ ). Similarly to galena, anglesite is not an acid-generating mineral. In this discussion, zinc and cadmium could be substituted for lead and form minerals analogous to anglesite.

Pyrrhotite ( $\text{Fe}_{1.0-x}\text{S}$ ) dominates over pyrite ( $\text{FeS}_2$ ) in the northeastern portion of the basin and, in combination with carbonates, helps avoid formation of acidic waters in this area. Pyrrhotite has only a small capacity to produce acidity to the extent that substitution for iron in the crystal structure occurs.

Mineral ores and their “typical” acid- or base-generating tendency are listed below.

Acid Generating:

- Pyrite ( $\text{FeS}_2$ )
- Chalcopyrite ( $\text{CuFeS}_2$ )
- Arsenopyrite ( $\text{FeAsS}$ )
- Jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ )
- Marcasite ( $\text{FeS}_2$ ) – orthorhombic dimorph of pyrite
- Tetrahedrite  $[(\text{Cu}, \text{Fe}, \text{Zn}, \text{Ag})_{12}\text{Sb}_4\text{S}_{13}]$
- Ferric sulfate  $[\text{Fe}_2(\text{SO}_4)_3]$
- Cation exchange

Base Generating (neutralize acidity):

- Calcite ( $\text{CaCO}_3$ )
- $\text{Fe}(\text{OH})_3$
- $\text{NaAlSi}_3\text{O}_8$
- Ankerite  $[\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2]$
- Quartz
- Cation exchange

Neither Acid- nor Base-Generating:

- Galena ( $\text{PbS}$ )
- Sphalerite ( $\text{ZnS}$ )
- Greenockite ( $\text{CdS}$ )
- Siderite ( $\text{FeCO}_3$ ) – effect becomes more basic with increasing substitution
- Pyrrhotite ( $\text{Fe}_{1.0-x}\text{S}$ ) – effect becomes more acidic with increasing substitution

As indicated, the two minerals with the greatest effect on pH are pyrite and calcite. The other minerals listed here are only expected to have proportionally small effects on pH. Calcite reacts to increase pH much more quickly than pyrite reacts to decrease pH. Thus, even where the acid-

generating potential of pyrite significantly exceeds the base-generating potential of calcite, it will take a long time (perhaps years) for the acid potential of pyrite to manifest itself fully.

### **Estimating Acidity of Sulfur-Containing Minerals**

The ability of laboratory methods (e.g., the Schafer and Sobek Method; Jennings and Dolhopf 1995) to indicate the potential acidity of sulfur-containing minerals is limited because of errors associated with trying to sequentially extract and differentiate nonacid and acid producing sulfur forms. A quick and approximate estimate of the acid-generating potential of an ore body can be made (Towatana 1990) by assuming the only sources of sulfate are ferric sulfate, lead sulfate, and zinc sulfate. Further, we must assume that all the ferric iron hydrolyses completely which will only occur when the pH is greater than, approximately, a pH of 5. The formula for ferric sulfate is  $\text{Fe}_2(\text{SO}_4)_3$ . Because each mole of ferric sulfate will generate 6 moles of hydrogen ions ( $\text{H}^+$ ), the following equation can be written.

$$\text{Moles hydronium (hydrogen) ions} = 2(\text{moles sulfate} - \text{moles zinc} - \text{moles lead}) \quad \text{Eq. 2}$$

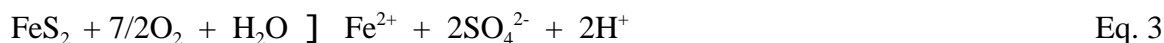
One mole of calcium carbonate will neutralize 1 mole of hydronium ions.

### **RELATION OF PYRITE/CARBONATE RATIOS TO PH AND DISSOLVED METALS CONCENTRATIONS**

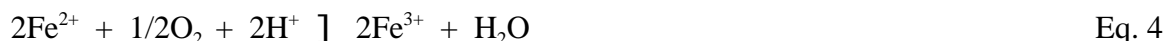
The geology and geochemistry of the host rock are some of the primary factors which affect the pH and composition of drainage from mine workings, tailings piles, waste rock and undisturbed mineralized areas. The wide ranging pH and metal concentrations found in the Coeur d'Alene mining district predominantly result from variable amounts of pyrite and carbonate minerals in the individual deposits and host rocks. The dominance of acid generating minerals (e.g., pyrite) results in acid pH values and the mobilization of metals into solution, whereas significant amounts of acid neutralizing minerals (e.g., calcite) increase the pH and can result in precipitation of oxides and hydroxysulfates that scavenge metals from solution (Balistrieri et al. 1999).

Varying quantities of pyritic ores and carbonate minerals exist throughout the Coeur d'Alene River basin. The following paragraphs illustrate how reactions written to describe the interactions of these deposits with the environment can be used to qualitatively estimate the range of pH values and dissolved metals concentrations found in the Coeur d'Alene River basin.

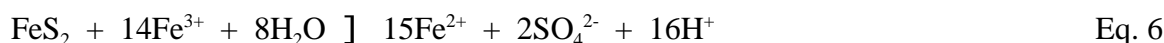
In pyritic ores formed under reducing conditions, sulfide is the dominant form of sulfur. Sulfides are unstable when exposed to oxygen. Exposure to oxygen can occur when the ores are mined and brought to the earth's surface or when contacted with groundwater containing dissolved oxygen. Contact with oxygen and water can oxidize and dissolve the pyrites as indicated by the following reactions (Stumm and Morgan (1970).



It is well recognized that oxidation of pyrite can produce acidic waters as shown in equation 3. In this reaction two moles of hydrogen ions ( $\text{H}^+$ ) are produced for each mole of pyrite oxidized resulting in increased acidity if not buffered by other minerals such as calcite. In this oxidation/reduction reaction, the sulfide is oxidized from the -2 to the +6 valence state while oxygen is reduced. The ferrous ion resulting from the oxidation of pyrite can subsequently be oxidized to ferric iron [Fe(III)] in the presence of oxygen as shown in equation 4.



Reaction 4 is considered the rate limiting step and is catalyzed by the bacterium *Thiobacillus ferrooxidans* (Singer and Stumm 1970). The resultant ferric iron may then precipitate as amorphous ferric oxyhydroxide (ferrihydrite) as illustrated in equation 5 or oxidize additional pyrite (equation 6).



Other minerals, such as jarosite [ $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ] or schwertmannite [ $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ ] could precipitate, instead of ferrihydrite, depending upon the specific pH and sulfate and ferric iron concentrations.

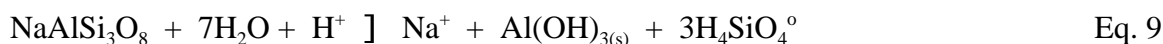
Figure G.5-1 is a pH-Eh diagram of the Fe-S- $\text{H}_2\text{O}$  system that shows the stability fields of various iron minerals. As indicated, pyrite is stable under reducing conditions. As the environment becomes more oxidizing, iron oxyhydroxide [ferrihydrite,  $\text{Fe}(\text{OH})_3$ ] becomes the stable phase. The small stability field for siderite in this diagram is somewhat misleading and the sizes of the various stability fields will change with different concentration and partial pressure of  $\text{CO}_2$  assumptions. Siderite is the predominant carbonate mineral found throughout the Coeur d'Alene River basin and is often associated with ore bodies. The important point to note regarding siderite is that it will form under reducing (e.g., subsurface) conditions at circumneutral



pH values. Stability fields for  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in this figure exist where iron minerals are relatively soluble and able to maintain solution concentrations of ferrous and ferric ions greater than  $10^{-6}$  M (approximately 0.06 mg/L). Iron oxyhydroxide  $[\text{Fe}(\text{OH})_3]$  readily forms above a pH of 4.0 under oxidizing conditions. Jarosite  $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$  becomes the stable mineral under highly oxidizing conditions with low pH values and sufficient sulfate. The diagram indicates that pyrite transformations occur as we encounter oxidizing conditions (higher Eh values). As shown in equation 3, this transformation can lead to increased acidity and, ultimately, increased metal concentrations.

Minerals with the capacity to release base and neutralize acid generated from pyrite oxidation are prevalent in the Coeur d'Alene River Basin. Balistrieri et al. (1999) cites Blowes and Sherlock when stating that these base-generating minerals, in order of reactivity are: calcite  $[\text{CaCO}_3]$ , dolomite  $[\text{CaMg}(\text{CO}_3)_2]$ , ankerite  $[\text{CaFe}(\text{CO}_3)_2]$ , oxides and hydroxides of Al and Fe, and aluminosilicates (feldspars, chlorite, and muscovite).

Three idealized reactions that represent the three general classes of base-generating minerals (carbonates, hydroxides of Al and Fe, and aluminosilicates) are provided, respectively in equations 7, 8, and 9. These reactions are idealized because some of these minerals may not exist as pure phases. For example, it has been shown that calcite can exist as a solid solution, with various elements (e.g., magnesium) substituting for calcium in the calcite crystalline structure.



In these reactions, one mole of hydrogen ions is consumed for each mole of reacted calcite (Equation 7) and albite (Equation 9) while three moles of hydrogen ions are consumed by the dissolution of one mole of ferrihydrite (Equation 8). Consumption of hydrogen ions will result in a rise in the measured pH value.

Balistrieri et al. (1999) used triangle diagrams to corroborate the fact that wide ranging pH values found in the Coeur d'Alene River Basin are the result of reactions involving pyrite oxidation, calcite or ankerite dissolution, and precipitation of ferrihydrite or mixtures of ferrihydrite and schwertmannite. In other words, the ranging pH values found in the Basin can be explained by

combinations of reactions 3 – 8. In this work, Balistrieri et al. (1999) estimated that the reacting pyrite/carbonate ratios ranged from near 0/1 to approximately 1/1.

Figures G.5-2 and G.5-3 are maps of pH values in surface waters and subsurface waters, respectively, from throughout the basin. Study of ore bodies and mineral deposits and concentrations reveals that high pH values are proximal to large concentrations of carbonates regardless of the presence or absence of large concentrations of pyrite. Conversely, low pH values are observed in the absence of large carbonate concentrations when pyrites are present. For example, the Prichard formation is argillite with relatively high concentrations of pyrite and low concentrations of carbonate. Consequently, in Pine Creek, which lies in the Prichard formation, lower pH values are observed. Conversely, the mouth of Canyon Creek and much of the mid-gradient area between Wallace and Osburn lie in the Wallace formation (relatively high carbonates) and these areas have relatively high pH values. Interestingly, the Wallace formation disappears before the Bunker Hill Tunnel, which exudes low-pH waters. Moreover, pyrrhotite ( $\text{Fe}_{1.0-x}\text{S}$ ) is more prevalent than pyrite ( $\text{FeS}_2$ ) in the northeastern portion of the watershed and, in combination with carbonates, helps preclude the formation of acidic waters in this area. Pyrrhotite does not generate acidity similarly to pyrite.

Figure G.5-4 is modified from Balistrieri et al. (1999) and is a plot of dissolved metals concentrations versus pH for aqueous samples collected from the Coeur d'Alene mining district. The samples were collected from mine adits and in seepage water from tailings piles. As would be expected, Figure G.5-4 illustrates that relatively lower pH values and higher dissolved metal concentrations occur when the ratio of reacting pyrite to carbonate deposits is high while circumneutral pH values and low dissolved metal concentrations are encountered when the reacting pyrite to carbonate ratios are low. However, the diagram indicates that high dissolved metal concentrations also can be found at near neutral pH values and result from deposits high in reacting pyrite and carbonate minerals. High metal concentrations and high pH values can result when iron oxyhydroxide is precipitated at a pH value unfavorable to metal adsorption. In this scenario, the iron is removed from solution but other metals are not concurrently removed.

Total dissolved metal concentrations (sum of dissolved Pb, Zn, Cd, Cu, Co, and Ni concentrations) in  $\mu\text{g/L}$  are plotted on Figure G.5-5 for CSM Units 1 and 2. As expected, as one moves down Canyon Creek, concentrations increase from 10.6  $\mu\text{g/L}$  near Burke to 4,701  $\mu\text{g/L}$  near the confluence with the South Fork. Concentrations are also increasing markedly as one begins to progress down Ninemile Creek. Sampling locations with dissolved metals are limited in Ninemile Creek because analyses were only conducted at a limited number of locations for all six metals.

In summary, inspection of pyrite and carbonate quantities can be used to qualitatively estimate the wide-ranging pH values and dissolved metal concentrations found throughout the Coeur d'Alene River basin (Figures G.5-2 to G.5-5). Equations 3 through 7 provide the theoretical foundation for these estimations. Figures in this section contain pH values and dissolved metals concentrations from locations throughout the Coeur d'Alene River basin. When these figures are compared, one can see that locations with low pH values exhibit high dissolved metals concentrations. Further, as Figures G.5-4 and G.5-5 indicate, either low or high dissolved metals concentrations can occur depending upon the relative concentrations of the pyrite and carbonate ores as discussed above.

## **WATER TYPES AND THEIR EFFECT ON METAL ATTENUATION/MOBILIZATION**

By evaluating water types (e.g., bicarbonate or sulfate) and major ion chemistry, one can determine if a water is, for example, merely mixing with another water or whether geochemical reactions occur that remove or add metals to the system. Additionally, these evaluations can indicate which reaches or locations are major contributors to water chemistry. Such information can be used to support of remedial alternatives to determine, for example, where to place a cutoff wall to prevent contaminated groundwater from entering surface waters.

### **Water Type Evaluation Methods**

Graphical methods, specifically Piper diagrams were used to help interpret water chemistry involving mixing. Piper or trilinear diagrams are non-linear in that the concentrations of major ions are normalized to the total cationic and anionic concentrations (Hem 1985; Paulson 1997, 1996). Therefore, because the concentrations are plotted as percentages, it is possible to have increases in concentrations that are not reflected in the diagrams.

Because bicarbonate and carbonate data were not directly available, a program was written in an excel spreadsheet to compute the bicarbonate and carbonate concentrations given the alkalinity and pH. This program also computed the degree of saturation of calcite with respect to each water sample. (See Appendix G.1 for equations used, a discussion, and other details.)

### **Water Type Evaluation Results**

Figure G.5-6 is a plot of the water types of the South Fork and Coeur d'Alene River from O'Brien Gulch, relatively near the headwaters of the South Fork, to Harrison at the confluence of the Coeur d'Alene River with Coeur d'Alene Lake. Tributary waters to the South Fork are

excluded from this plot which represents surface waters during a high-flow event in 1999 (Woods 2000). Because cations plotted essentially in the same location on the diagram, only the anion portion is shown for greater resolution.

From Figure G.5-6, it can be noted that surface waters of the main stem of the South Fork and Coeur d'Alene River remained bicarbonate rich with a few exceptions. For example, the water types at the two sampling stations located at Smelterville and Pinehurst are noticeably different from other surface waters in the South Fork and Coeur d'Alene River because of a significantly higher sulfate component. Movement of the South Fork through the Bunker Hill Superfund site changed the water type to a more sulfate-rich water indicating major contributions to surface-water chemistry in this area. The waters have started to move toward a greater contribution of sulfate at Big Creek and Kellogg. Big Creek and Kellogg water types lie at the top of the cluster of water types on Figure G.5-6. After Pinehurst, the surface waters revert to their former bicarbonate character because of the volume of water contributed by the North Fork, a predominately bicarbonate water.

The change in water types is even more pronounced during a low-flow event (see Figure G.5-7) in 1997 (URS 2000) because of the lack of dilution experienced during high flows. The samples begin at O'Brien Gulch (SF 205) and progress down the South Fork to Pinehurst (SF 272). The two samples lying at the top of the plot are from stations near Smelterville (SF 270) and Pinehurst (SF 271). As seen in Figure G.5-7, movement through the Bunker Hill Superfund Site has changed the water type of the South Fork from predominately bicarbonate to one that is predominately sulfate. Also, note the relatively steady progression of water type from bicarbonate to sulfate as one moves from O'Brien Gulch (SF 205) to Pinehurst (SF 271). These samples lie at the bottom (O'Brien Gulch) and top (Pinehurst) of the diamond shown in Figure G.5-7.

In summary, based on the Piper diagrams, examination of water types indicates reaches where water chemistry changes noticeably due to loading of specific chemicals (e.g., sulfate at the Bunker Hill site). Barton (2000) studied interactions of groundwater and surface water at certain locations within the Coeur d'Alene basin. Further investigations need to be undertaken to resolve possible contributions of groundwater.

## **RELATIONSHIP BETWEEN IRON AND ASSOCIATED METAL CONCENTRATIONS IN SURFACE WATER**

Knowledge of the association between iron and a metal allows one to predict the conditions under which metals may be released into the dissolved phase. Iron is important because it can

change the pH of water as it loses or gains electrons and precipitates or dissolves in the oxide or sulfide mineral state. Metals also adsorb/coprecipitate with iron, decreasing solution concentrations of dissolved metals. Further, given a change in the redox condition or pH, the iron may dissolve releasing metals into solution.

Correlation coefficients (r-values) were calculated to measure the linear relationship between total iron and total concentrations of lead, zinc, and cadmium. A high correlation (value close to 1.0) indicates a strong positive linear relationship between iron and another metal. Correlation does not imply causation but given a high positive correlation, we infer that the metal is adsorbed, coprecipitated, or precipitated (associated) onto or with the iron. If it can be shown that metals tend to be preferentially associated with iron, this information can be used to determine optimum conditions for implementation of a remedial alternative. For example, stabilization to a different pH value may be required to immobilize metals associated with iron as opposed to metals associated with other particulates such as silts and clays.

Generally, in the high-flow event of 1999 (Woods 2000), a moderate to strong positive correlation existed between total iron and total concentrations of lead, zinc, and cadmium. Table G.5-1 contains correlation coefficients between pH and total metal concentrations for 42 samples (South Fork and tributaries) collected by the U.S.G.S. (Woods 2000). The correlation coefficient (r-value) was stronger (0.62) between total iron and total lead than between total iron and total zinc (0.42) and total cadmium (0.21) which agrees with the observation that lead predominantly migrates in the particulate form. Zinc and cadmium are known to exist primarily in the dissolved phase and the lower correlation coefficients for zinc and cadmium than for lead support this observation. In certain reaches of the South Fork and Coeur d'Alene River (e.g., Pinehurst to Harrison), the correlation between total iron and total concentrations of individual metals reached 0.97 (lead), 0.95 (zinc), and 0.93 (cadmium). Analytical data suggest a higher percentage of lead is found in particulate (total) form than either zinc or cadmium. These correlation coefficients further suggest that metal association with particulate iron is important.

A positive correlation existed between iron and manganese (0.78) and, therefore, between manganese and total concentrations of lead (0.71), zinc (0.45), and cadmium (0.27). Again, these correlation coefficients support observations that lead tends to be associated with metal oxides (e.g., iron and manganese) to a greater degree than zinc and cadmium.

McCulley, Frick & Gilman (1991) noted a high positive correlation (r-value of 0.89) between lead and total suspended solids during another high-flow event. However, they did not analyze for iron and, therefore, a similar relationship with iron could not be established.

In contrast to the above, during low-flow events (e.g., 1997, URS 2000; MFG 1992), weak to negative correlations existed between total iron and total concentrations of lead, zinc, and cadmium (Table G.5-2). The correlation coefficients, in this low-flow event, between total iron and total concentrations of metals, ranged from 0.15 for lead to -0.07 for cadmium and -0.09 for zinc.

Correlations support observations that metals tend to be associated with particulate iron and, also, that they are more often associated with particulate iron during high-flow events than in a low-flow events. Further, correlations support the hypothesis that particulate forms of iron scavenge metals, especially lead. Caution must be exercised in generalizing to the Coeur d'Alene River basin conclusions obtained from a particular high-flow event and a particular low-flow event.

In summary, a high-flow event and a low-flow event were analyzed to evaluate the linear correlations between total iron and the total concentrations of metals. Metals tended to be more strongly associated with particulate iron during the high-flow event than the low-flow event. There was a stronger correlation between total iron and total lead than between total iron and other metals (total zinc and total cadmium) during the high- and low-flow events. This information can be used to help select the optimum conditions for implementation of a remedial technology.

## **DISSOLUTION/PRECIPITATION**

Dissolution and precipitation of solid phases can be important mechanisms for release or immobilization of metals and guide in the selection of remedial alternatives. For example, precipitation of lead phosphates may remove lead to low concentrations when employed in reactive barrier walls. Additionally, knowledge of the dissolution/precipitation reactions that occur in surficial and submerged sediments in the Lateral Lakes and Coeur d'Alene Lake will help determine how these sediments are addressed in the Feasibility Study.

The ion-speciation-solubility portions of the MINTEQ geochemical computer code (Felmy et al. 1984) were used to model selected aqueous solutions. In the speciation submodel, MINTEQ computes the activities of complexed and uncomplexed cationic and anionic species, neutral ion pairs, and the activities of cationic and anionic redox species. These activities are then fed to the solubility submodel (Peterson et al. 1987). The solubility submodel performs solubility calculations in which ion activity products (AP) for solids and minerals are calculated. The activity products are compared to the solubility products (K) of minerals and solids stored in the

thermodynamic data base of MINTEQA2 to develop a saturation or disequilibrium index [ $\log (AP/K)$ ]. This saturation index (SI) indicates the degree of undersaturation or oversaturation of a solid relative to solids and minerals of interest.

The highest dissolved lead concentration observed in the high-flow synoptic sampling study by the U.S.G.S. (Woods 2000) was 35.6  $\mu\text{g/L}$  at the mouth of the East Fork of Ninemile Creek. Computations of saturation indices in surface waters throughout the basin using the MINTEQA2 geochemical computer code (Allison et al. 1991) indicated undersaturation with respect to plausible solid-phase controls for zinc, and cadmium in the high-flow event. The plausible solid-phase controls evaluated by the model included sulfates, carbonates, hydroxides, hydroxycarbonates, and phosphates. Lead was undersaturated with respect to the same possible solid-phase controls except for a lead phosphate. Pyromorphite with the formula  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$  was oversaturated (S.I. of 0.89) with respect to its dissolved components and could help maintain phosphate concentrations at low levels. Consequently, with the exception just mentioned and, possibly one other discussed below, precipitation of mineralogical forms of lead, cadmium, and zinc is not expected to act as a removal mechanism in surface waters of the South Fork, North Fork, Main Stem Coeur d'Alene River, Spokane River or at the mouths of tributaries during high-flow events. Conversely, as these waters migrate through reaches where mineral forms of lead, zinc, and cadmium are present due to evaporation and precipitation, mineralogical forms of lead, zinc, and cadmium are expected to dissolve and release metals to solution.

In the low-flow event (1997, URS 2000), the highest dissolved lead concentration was only 23.9  $\mu\text{g/L}$ . In this sampling event, where dissolved metal and major ion concentrations were generally higher, lead was undersaturated with respect to known plausible solid phases and would not be expected to precipitate from solution. Phosphate was not included in these solution analyses and, therefore, possible precipitation of phosphoric forms of lead could not be evaluated. Otavite (cadmium carbonate) may precipitate from solution at certain locations and control solution concentrations of cadmium. Precipitation/dissolution of otavite may help explain the generally relatively low concentrations of this metal (compared to lead and zinc) observed throughout the basin.

Lead may precipitate from solution as a lead hydroxycarbonate (hydrocerrusite) if dissolved concentrations exceed 4,000  $\mu\text{g/L}$  at pH 4 and approximately 200  $\mu\text{g/L}$  at pH 8 (USEPA 1999a; Rhoads et al. 1992). As noted in the preceding paragraph, in the presence of phosphate and chloride these solubility limits may decrease appreciably. Because the highest dissolved lead concentrations observed in the high-flow (1999, Woods 2000) and low-flow events (1997, URS 2000) were 35.6  $\mu\text{g/L}$  and 23.6  $\mu\text{g/L}$ , respectively, this common mineral, hydrocerrusite,

generally is not expected to act as a lead solubility control in surface waters of the Coeur d'Alene River basin.

Iron oxyhydroxide was predicted to precipitate and can concurrently remove metals from solution through adsorption. The solutions analyzed in the high- and low-flow events were oversaturated with respect to amorphous ferric oxyhydroxide (ferrihydrite). The log of the saturation index was usually close to 1.2 or higher in every case. Oversaturation with ferrihydrite might be explained by part of the operationally-defined dissolved iron actually existing in colloidal form similarly to lead as evidenced by the U.S.G.S. study (Woods 2000). Oversaturation conditions indicate that amorphous iron should be precipitating from solution and helping to maintain dissolved ferric iron at low concentrations. In the adsorption section, adsorption of metals onto this precipitated iron is presented. The importance of iron precipitation can depend on the pH regime at which the iron is precipitating. If iron precipitates in relatively low pH water (4-5), the iron will be removed from solution before a favorable position on the adsorption isotherm for metals is reached. In this scenario, high metal concentrations at circumneutral pH values ensue. If the pH at which iron precipitates is sufficiently high, metals will adsorb (see Figure G.5-8) onto the precipitating iron and be removed from solution.

All solutions were undersaturated with respect to common minerals such as calcite ( $\text{CaCO}_3$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), anglesite ( $\text{PbSO}_4$ ), rhodochrosite ( $\text{MnCO}_3$ ), amorphous zinc hydroxide [ $\text{Zn}(\text{OH})_2$ ], and otavite ( $\text{CdCO}_3$ ). Certain of the solutions were near equilibrium to slightly oversaturated with respect to quartz and  $\text{ZnSiO}_3$  but it is not expected that these solids are controlling the concentrations of certain of their dissolved components. Quartz is a crystalline form of  $\text{SiO}_2$  and it is anticipated that amorphous forms of  $\text{SiO}_2$  should initially precipitate and gradually "age" to form quartz. It is possible, however, that a less crystalline form of silicon dioxide is dissolving and helping maintain silica concentrations in solution. As for  $\text{ZnSiO}_3$ , we are not aware of this solid readily precipitating in the environment. Lindsay (1979) at one time speculated (based on thermodynamic constraints) that  $\text{ZnSiO}_3$  in conjunction with  $\text{SiO}_2$  controlled zinc concentration in soils but later concluded their thermodynamic data were incorrect.

Dissolution/precipitation reactions are of minor importance in surface waters of the Coeur d'Alene basin. Dissolution/precipitation reactions are expected to be of greater importance where chemical nonequilibrium exists. Examples of areas of chemical nonequilibrium are likely to be found at seeps and adits where high contaminant concentrations and/or steep pH and redox gradients exist. Precipitation at seeps can reduce metal concentrations through direct precipitation of the metal or as the metal adsorbs onto precipitated iron. Additionally, dissolution/precipitation reactions become of paramount importance in porewaters of subsurface



sediments found in the Lateral Lakes and Coeur d'Alene Lake. Knowledge of precipitation/dissolution reactions in subsurface sediments will impact how these sediments are addressed in the feasibility study.

## **ADSORPTION/DESORPTION**

Modeling (surface complexation approach) to predict the adsorption of zinc, lead, and cadmium was conducted for two principal reasons. First, to determine if the percentages of dissolved and particulate metals in solution could be explained by metal adsorption onto ferric oxyhydroxides. Second, if metals appear to be primarily associated with iron oxyhydroxides in solution, to predict the optimal pH regime for stabilizing the metals. Furthermore, if such a model is applicable, it may be possible to determine how iron releases or attenuates metals as the pH or solution composition change as metals associated with iron are transported throughout the basin.

Adsorption is usually thought of as attenuation of an adsorbate (e.g., metal ion) by the surface of a preexisting adsorbent (e.g., iron oxyhydroxide). Often a debate occurs as to whether a metal is being removed because of adsorption onto or coprecipitation with iron. There is no justification in making this distinction. Coprecipitation is the removal of other metals or species from solution by precipitation of a solid phase. Metals or species are removed from solution by physical entrapment, surface adsorption, or substitution into the crystal lattice. Equilibrium thermodynamics does not distinguish between the effect of reagent sequence additions on precipitation and neither does this document. In fact, Leckie et al. (1980) found adsorption and coprecipitation indistinguishable in a study of the removal of Cd, Zn, Cu,  $\text{SeO}_3$ , and  $\text{CrO}_4$  from solution by ferric oxyhydroxides. Accordingly, from the perspective of iron sequestering metals in the Coeur d'Alene River basin, the order of reagent additions has no effect on adsorbate removal efficiencies. In other words, it is not important to metal removal whether iron oxyhydroxides already exist when they contact metal-laden solutions in the Coeur d'Alene River basin or whether iron precipitates from solutions containing the metals; the effective metal removal will be the same.

Surface complexation models (e.g., MIT Diffuse-Layer Model) have the potential to accurately predict variations in oxide acid/base properties as a function of ionic strength and pH. Numerous adsorption studies have demonstrated increased adsorption of lead with increasing pH (U.S. EPA 1999a and b). Empirical approaches, such as the distribution coefficient and Freundlich isotherms, are limited to particular conditions and are not easily extrapolated to other conditions of pH and ionic strength. Estimation of distribution coefficients for lead, cadmium, and zinc are included in Appendix G.3.

Models, such as the surface complexation approach, are based on chemical theory and enable equilibrium adsorption beyond the range of available data. Metal adsorption to oxide surfaces (such as amorphous oxyhydroxide) is analogous to metal hydrolysis in solution in that both adsorption and hydrolysis increase as the pH is increased and both are accompanied by the release of protons. Cations have highly pH-dependent adsorption edges. The affinity of a metal for adsorption decreases with increasing adsorbate/adsorbent ratios.

The MIT Diffuse-Layer Model was used to model adsorption in the surface waters of the Coeur d'Alene River basin because it fits the data equally as well as other surface complexation models (e.g., Constant Capacitance and Triple-Layer Models), while eliminating multiple planes of adsorption and multiple fitting parameters. In the Diffuse-Layer Model, adsorption takes place in one layer and a Gouy-Chapman diffuse layer is assumed for the solution side of the interface.

Adsorption of ions on oxide surfaces is a two-step process. There is a rapid initial uptake (seconds-minutes) followed by a slower step (hours-weeks) in which equilibrium is asymptotically approached. If the number of surface sites is in excess, equilibrium is achieved rapidly. In natural waters, the assumption of equilibrium is valid in most circumstances and was assumed valid for the adsorption modeling conducted in this document. In this discussion, other terms, such as "associated with" or "particulate forms," are sometimes used in lieu of the word "adsorbed."

Data from low-flow (1997, URS 2000) and high-flow events (Woods 2000) were used to model the percent adsorption of metals onto iron oxyhydroxides. As mentioned, the adsorption model selected was the MIT Diffuse-Layer Model (DLM) developed by Dzombak (1986).

Lead adsorption was predicted most accurately by the model (Tables G.5-3 and G.5-4). In general, the predicted values follow the general trends for the measured data. That is, predicted values tend to increase or decrease as the measured values increase or decrease. Because some of the iron may be associated with colloids which were not determined, it is impossible to know with exactitude the measured percentages of adsorbed and dissolved metals.

For the low-flow event, the predicted values for lead followed the measured adsorption trends. The prediction of minimal adsorption of zinc and cadmium was confirmed by the measured values. In the high-flow event, where more total iron and metals are re-suspended, predictions of lead adsorption were always greater than 90 percent as were the measured adsorption percentages, with one exception. For the high-flow event, the predicted percentages of adsorbed zinc and cadmium were sometimes higher and sometimes lower than the measured values.

In summary, the percentages of lead, zinc, and cadmium in the dissolved phase could be explained, to a large extent, by metal adsorption onto iron oxyhydroxides (Tables G.5-3 and G.5-4). Second, if metals are associated primarily with iron oxyhydroxides, optimal pH regimes for metal stabilization were approximately >6.0, 8.0, and 9.0 for lead, zinc, and cadmium, respectively (see Figure G.5-8). These predictions of percent metal adsorbed versus pH were based on the water chemistry analyzed at Trowbridge in May 1999 during a high-flow synoptic sampling event. Changes in the relative or absolute metal concentrations will modify these adsorption isotherms (Figure G.5-8). Additionally, it is recognized that, in addition to iron oxyhydroxides, other materials (e.g., organic material) may provide adsorption surfaces for metal adsorption.

## **OXIDATION/REDUCTION REACTIONS IN LATERAL LAKES AND COEUR D'ALENE LAKE SEDIMENTS**

Coeur d'Alene Lake is oligotrophic with dissolved oxygen found throughout the water column except for particular areas of the lake during certain times of the year. This oxygen will diffuse into the upper few centimeters of the lake bottom causing an oxidizing zone to exist in the upper portion of the bottom sediments. Sediments found deeper in the sediment profile because of deposition subsequent to their placement, become more reducing and metal oxides begin to dissolve. Geochemical reactions controlling metal mobilization in the near surface sediments is presented in this section.

### **Determination of Sediment Oxidation/Reduction Conditions.**

#### ***Lateral Lakes***

Rabbi (1994) collected sample cores from 8 lateral lakes and at inlets to the lakes. The sediments were generally fine grained and rich in organic matter in the upper portion of the sediment profile. Bull Run Lake sediments had the highest maximum concentrations of lead (27,200 mg/kg), zinc (20,600 mg/kg), and cadmium (197 mg/kg) while the lowest maximum concentrations of lead (3,610 mg/kg), zinc (3,610 mg/kg), and cadmium (24 mg/kg) were encountered in Rose Lake. The foregoing concentrations were purportedly several orders of magnitude higher than concentrations identified in Bells Lake, an uncontaminated lake found in the valley of St. Joe River in similar geologic materials. Hoffman (1995) studied two of the lateral lakes, Medicine and Thompson, and concluded, based on evaluation of  $^{137}\text{Cs}$ , that 14 centimeters of sediments were deposited between 1951 and 1964 (13 years) while only 10 to 12 centimeters were deposited between 1964 to 1992 (28 years). Obviously, the deposition rate is

decreasing which has implications regarding how fast deposited material might be buried and reduced to sulfides. Given the relatively high metals concentrations in sediments, Rabbi (1994) attributes the relatively low solution concentrations to high pH values (6.4 to 7.5) and to their association with sulfides, carbonates, metal oxides (iron and manganese), clay, organic matter, and hydroxides. Rabbi (1994) found the majority of the metals were partitioned into oxide, organic, and, in lesser amounts, to carbonate phases. Residual phases and exchange sites did not sequester appreciable quantities of metals.

Wet sieving and centrifuging techniques were used by Hoffman (1995) to separate sediment cores from Thompson and Medicine Lakes into various particle sizes. The most abundant size fraction (silts) had the lowest metal concentrations while the least abundant fraction (clays) had the highest metal concentrations. Knowledge of which size fraction is associated with the highest metal concentrations has implications for remediation. The medium-clay size fraction (0.2 to 0.08  $\mu\text{m}$ ) contained the highest concentrations of lead in all depth intervals while the coarse-clay size fraction (<0.2 to 2.0  $\mu\text{m}$ ) contained the largest absolute mass of lead. For cadmium, the highest concentrations and largest absolute mass were found in the fine-clay size fraction (<0.08  $\mu\text{m}$ ). With respect to zinc, the highest concentrations were encountered in the fine-clay size fraction (<0.08) and the largest absolute mass was found in the coarse-clay (0.2 to 2.0  $\mu\text{m}$ ) and medium-silt (5 to 20  $\mu\text{m}$ ) size fractions.

A striking feature of the preceding discussion is the quantity of metal-containing particulates that would be classified as dissolved based on passing a 0.45  $\mu\text{m}$  filter. The highest concentrations of lead, zinc, and cadmium were found in size fractions that would pass a 0.45  $\mu\text{m}$  filter and would, therefore, be classified as dissolved metals. Because of the breaks in sizes, it is impossible to determine the absolute mass that would pass a 0.45  $\mu\text{m}$  filter for each metal. However, a large percentage of each metal found on these sediments would be classified as dissolved.

Rabbi (1994) performed sequential extractions on 13 sediment cores using procedures widely accepted (Tessier et al. 1979). This method purports to partition minerals into five fractions. Most of the zinc was partitioned into the oxide and organic carbon phases with a lesser quantity being associated with carbonates. Partitioning of lead was onto the oxides, carbonates, and organic phases in order of prominence. The major part of the lead in Medicine Lake was associated with the organic phase followed by oxides and carbonate. In general, lead, zinc, and cadmium were associated with the following minerals in decreasing order of importance: oxide > carbonate > organics > exchangeable > residual. Up to 64 percent of the lead, up to 76 percent of the zinc, up to 71 percent of the arsenic, and up to 57 percent of the cadmium were purportedly associated with the oxide phase. As noted, the Tessier et al. (1979) method is designed for

aerobic sediments and, therefore, does not consider sulfides. Further, handling procedures to prevent oxidation of sulfide minerals are, therefore, not required.

Rabbi (1994) speculated that sulfides were forming at deeper depths under anoxic conditions and that iron and manganese were reduced under these conditions with the concomitant release of metals. It is doubtful that lead, zinc, or cadmium precipitate as hydroxides at the pH values and metal concentrations found in these waters. A single sample from Medicine Lake was examined under an electron microscope and indicated that most of the lead was associated with sulfides and that free sulfur was present in the sediments.

To examine the hypothesis that solids could be precipitating or dissolving as the redox potential changes in sediments, a water sample collected from 56 to 58 cm in Medicine Lake was evaluated. This sample was selected because of the extremely high metal concentrations measured. If solids will not precipitate at elevated metal concentrations, it is unlikely they will precipitate at lower concentrations. The concentrations of lead, zinc, and cadmium in this sample were 2,540 µg/L, 10,090 µg/L, and 1,120 µg/L, respectively. Concentrations of other species were taken from the May, 1999 sample collected at Rose Lake. The pH was fixed at 7.0 and the Eh was allowed to vary in 60 millivolt increments in a computer model simulation of redox change.

The initial redox value was fixed at 260 millivolts to simulate the redox condition of sediments closer to or at the sediment/water interface. At this Eh and an initial iron concentration of 20 µg/L, an amorphous ferric oxyhydroxide (ferrihydrite) was stable (slightly oversaturated) and would have a tendency to precipitate. Similarly to conditions encountered in surface waters of the South Fork and the Coeur d'Alene River, a quartz mineral with a crystallinity between quartz and amorphous silicon dioxide could be controlling silica concentrations in solution. Quartz is unaffected by the change in redox potential and its precipitation/dissolution status remained constant throughout the simulations. Willemite ( $\text{Zn}_2\text{SiO}_4$ ) was near equilibrium and could be controlling solution concentrations of zinc while otavite has the potential to precipitate and affect cadmium concentrations. A lead carbonate (cerrusite) was oversaturated with respect to solution concentrations of lead and could affect lead concentrations in solution.

As the redox potential was lowered to approximately 200 millivolts, ferric oxyhydroxide began to dissolve in the modeling simulations and willemite, otavite, and cerrusite became less oversaturated. As the redox potential continued to fall, willemite, otavite, and cerrusite became undersaturated and dissolved. Between an Eh (measure of redox potential) of -80 and -137 millivolts, sulfides of lead (galena), zinc (sphalerite), and cadmium (greenockite) are predicted to precipitate.

In summary, this illustrates that (at least at high metal concentrations and a sulfate concentration of 3.1 mg/L) metals in the lateral lakes could precipitate as oxides and carbonates. As these sediments are moved deeper into the sediment profile, conditions become more reducing. This would eventually cause dissolution of ferric oxyhydroxide and metal carbonates with concurrent metal release. As the redox potential continues to fall, metals can precipitate authigenically as their corresponding sulfides (e.g., galena, PbS).

### *Coeur d'Alene Lake*

Waters immediately overlying Coeur d'Alene Lake sediments are generally oxygenated (Woods and Beckwith 1997). Lake sediments within a few centimeters of the sediment water/interface are anoxic. The latter conclusion is supported by Balistrieri (1998), Harrington et al. (1998), Horowitz et al. (1993) and Horowitz (2000). There is a well-defined reduction sequence of inorganic oxidants as they are reduced by oxidation of organic matter. This sequence is oxygen, nitrate, Mn oxyhydroxides, Fe oxyhydroxides, and sulfate. Balistrieri bases her conclusions of anoxic sediments within a few centimeters of the sediment/water interface on observations of these oxidant reduction reactions. Harrington et al. (1998) took redox measurements with a platinum electrode (corrected to the SHE electrode) and found most measurements to be well below 0 millivolts which is indicative of anaerobic conditions. Most probable number estimates of sulfate-reducing bacteria (Harrington et al. 1998) indicated numbers ranging from  $10^4$  to  $10^6$  cells/g wet weight sediment. These bacteria are supportive of the conclusion that anaerobic conditions exist. Horowitz noted gas bubbles arising from lake sediments and further observed a reddish-brown coloring develop on samples taken from the lake and exposed to oxygen. This would indicate that ferrous iron is oxidizing to ferric iron. The presence of ferrous iron is supportive of suboxic conditions.

Horowitz et al. (1993) performed a 2-step sequential extraction on the upper 2 cm of lake sediments and found a majority of the metals to be associated with an operationally-defined oxide phase (Fe, Mn, Al). This is in general agreement with Harrington et al. (1998) who concluded that anaerobic conditions were encountered below approximately 4 cm. Harrington et al. (1998) collected samples 8 cm long; therefore surface sediments were mixed with subsurface sediments. Sulfate pore-water concentrations (Balistrieri 1998) collected by the U.S.G.S. generally decrease in concentration with increasing sediment depth. This finding, coupled with redox measurements, suggests that sulfate reduction is occurring.

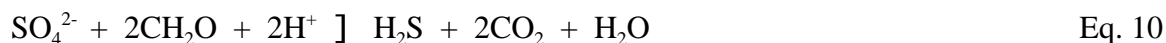
## Geochemical Model of Metal Fate in Coeur d'Alene Lake

Based on the above, the following geochemical model of metal fate in Coeur d'Alene Lake is proposed. The total and dissolved iron concentrations measured in the Coeur d'Alene River are predominately in the ferric state (oxidized form). These surface waters are exposed to oxygen and if iron existed in the ferrous state, higher dissolved iron concentrations would be expected. Further solubility calculations indicate oversaturation with respect to ferric oxyhydroxide (ferrihydrite).

Correlations and surface adsorption modeling performed on iron and metal loads in the Coeur d'Alene River suggest a considerable quantity of trace metals is associated with iron particulates. Some of these particulates are swept into Coeur d'Alene Lake where they settle through the water column and rest on the bottom. Dissolved iron, entering the lake from the Coeur d'Alene River, may also precipitate in response to water chemistry changes within the lake and settle on the bottom. In addition, other metal sequestering materials such as manganese and aluminum oxides and organic carbon enter the lake concomitantly with iron, bringing adsorbed metals. These materials also have a tendency to settle out of the water column.

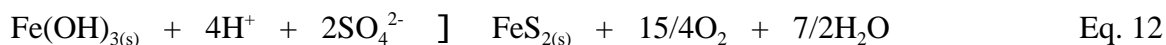
Oxygenated water immediately overlying sediments communicates with pore water in the upper 4 cm or less of the sediments mainly through gaseous diffusion processes. This communication helps maintain oxides in the uppermost portion of the sediments as Horowitz et al. (1993) has observed. As additional sediment deposition occurs, the sediments are buried more deeply and are farther from the sediment-water interface. Eventually, as the sediment deposition depth increases, their redox environment changes from aerobic to suboxic to anaerobic.

Assuming carbon is the reactive organic phase and exists in the zero valence state, one mole of sulfate will precipitate one mole of metals based on the reaction stoichiometry of equations 10 and 11.



where M represents a divalent metal (e.g., Pb, Zn, or Cd)

Precipitation of iron as an iron sulfide will engender a rise in pH as shown in equation 12 because of the consumption of hydrogen ions ( $H^+$ ). The average pH of subsurface sediments, where reaction 12 would be expected to take place, was higher (6.4) than the average pH of surface sediments (5.5) (Harrington et al. 1998).



Because of oxidation/reduction reactions such as those discussed in the preceding paragraphs, a diagenetic cycling of metals takes place and redox-sensitive elements, such as iron, manganese, and arsenic, are most abundant near the sediment/water interface (Harrington et al. 1998).

In summary, metals within 2 to 4 cm below the sediment/water interface are predominately associated with iron oxides (Horowitz et al. 1993). Because of reducing conditions below 4 cm (if not higher), metal oxides of iron and manganese are not stable. Metals encountered below 4 cm of the sediment/water interface are primarily found in association with sulfides and organic carbon (Harrington et al. 1998; Balistrieri 1998). If an anoxic hypolimnion developed as a consequence of eutrophication, metals found in the upper 2 to 4 cm could be released to the water column as long as conditions are not reducing enough to convert sulfate to sulfide. Metals encountered below 4 cm would not be affected significantly. The released metals (upper 4 cm), including iron, would migrate until encountering dissolved oxygen higher in the water column, at which time, the iron would reoxidize and precipitate as iron oxyhydroxide. Metals could then readsorb onto the precipitated iron oxyhydroxides. The precipitated material would settle until encountering the anoxic zone, where dissolution would reoccur. Recycling would continue as long as anoxic and oxic zones existed. During the recycling process, metals would migrate according to natural hydraulic and concentration gradients in the lake modified by anthropogenic disturbances such as boating and water-level controls through the Post Falls dam. As has been suggested (Woods and Beckwith 1997), nutrient control measures are the most direct means for preventing eutrophication.



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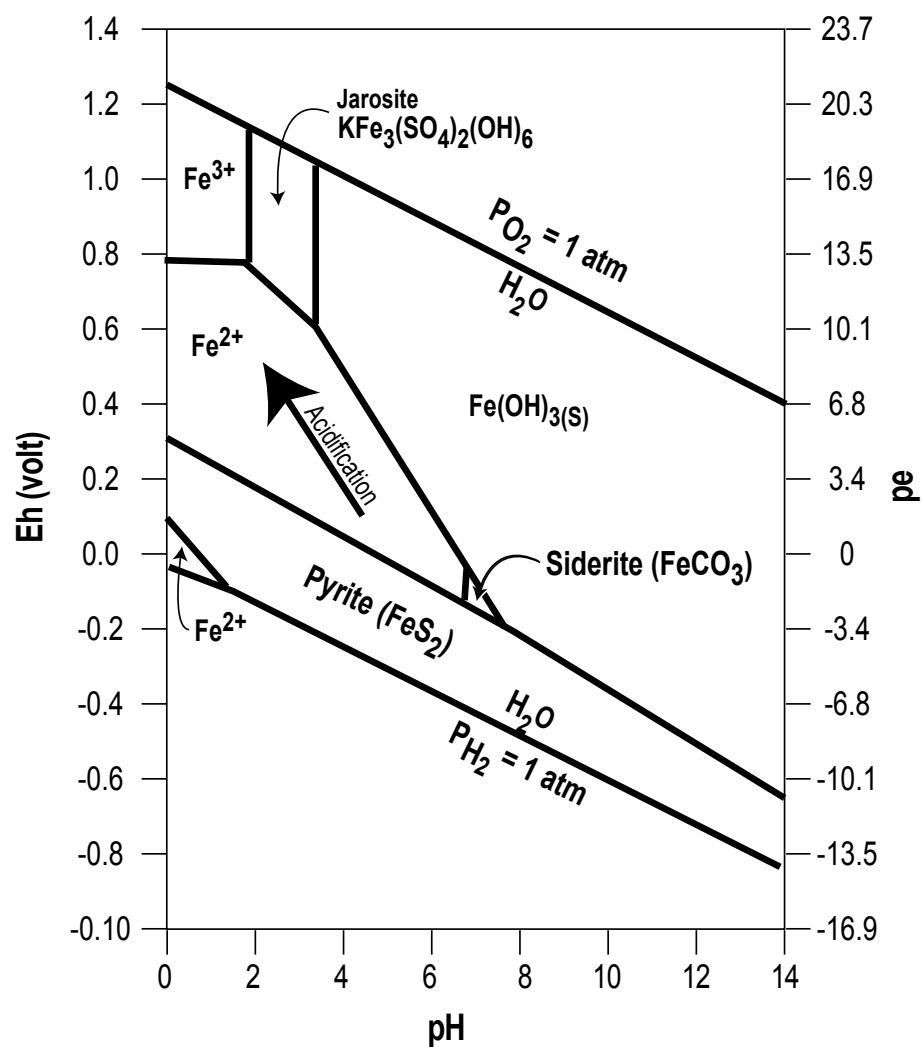
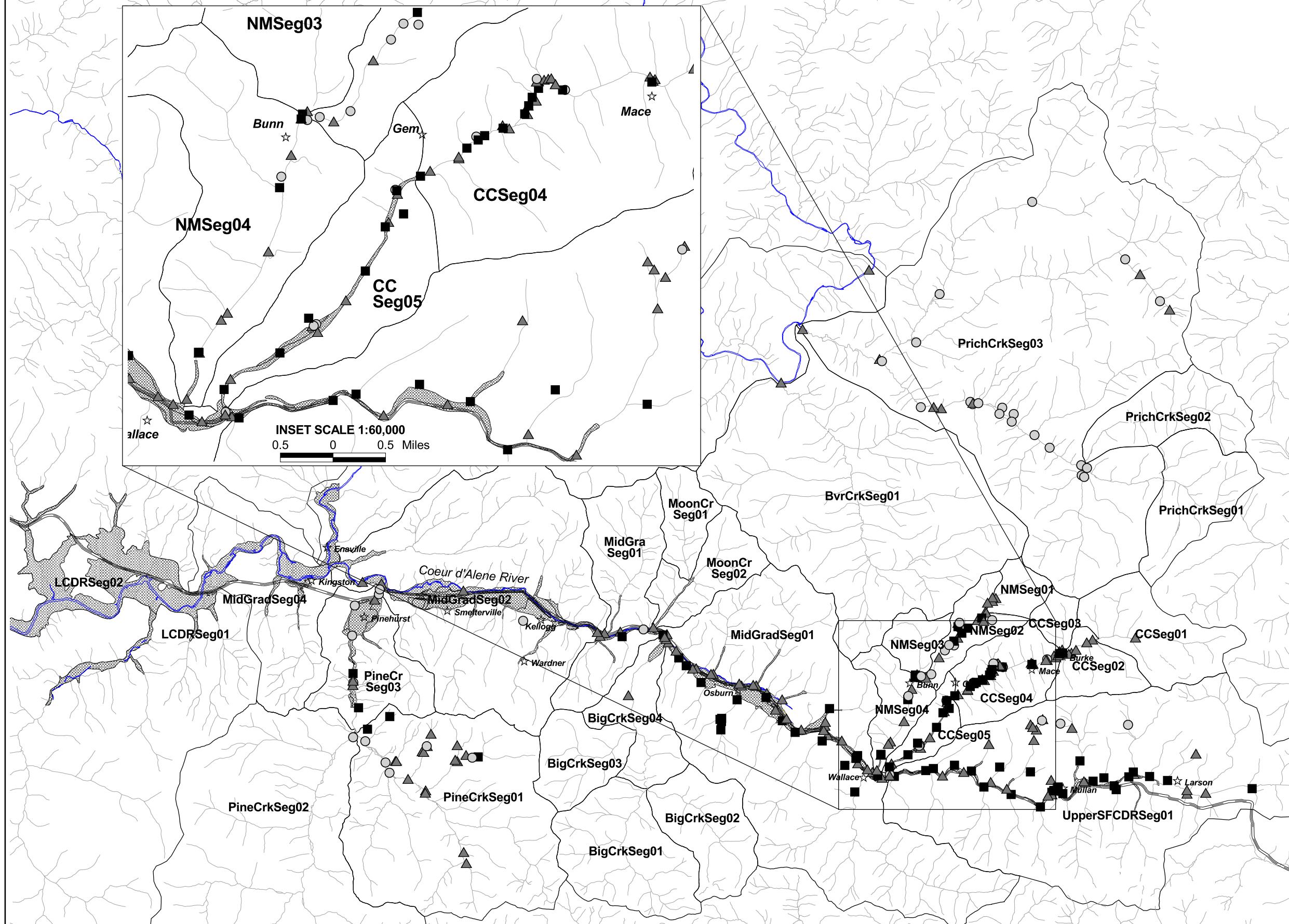


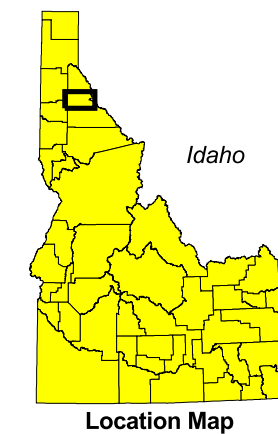
Figure G.5-1  
Stability Fields at the Fe-S-H<sub>2</sub>O System.  
( $A_s = 10^{-2} \text{ Mol}$ ,  $\text{PCO}_2 = 0.01 \text{ atm}$ )

Figure G.5-2  
pH Values Found in Surface Waters



LEGEND

- pH Range**
- 3.4-6.2
  - △ 6.2-7.2
  - 7.2-8.9
- Stream
- Interstate 90
- City
- River Segment Boundary
- River/Lake/Floodplain



NOTES

- 1) Base map coverages obtained from the Coeur d'Alene Tribe, URS Greiner, Inc., CH2M HILL, and the Bureau of Land Management.
- 2) Sampling locations obtained from URS Greiner, Inc., Technical Data Management database as of 10/16/99.

SCALE 1:180,000  
1 0 1 Miles

027-RI-CO-102Q  
Coeur d'Alene Basin RI/FS  
RI REPORT

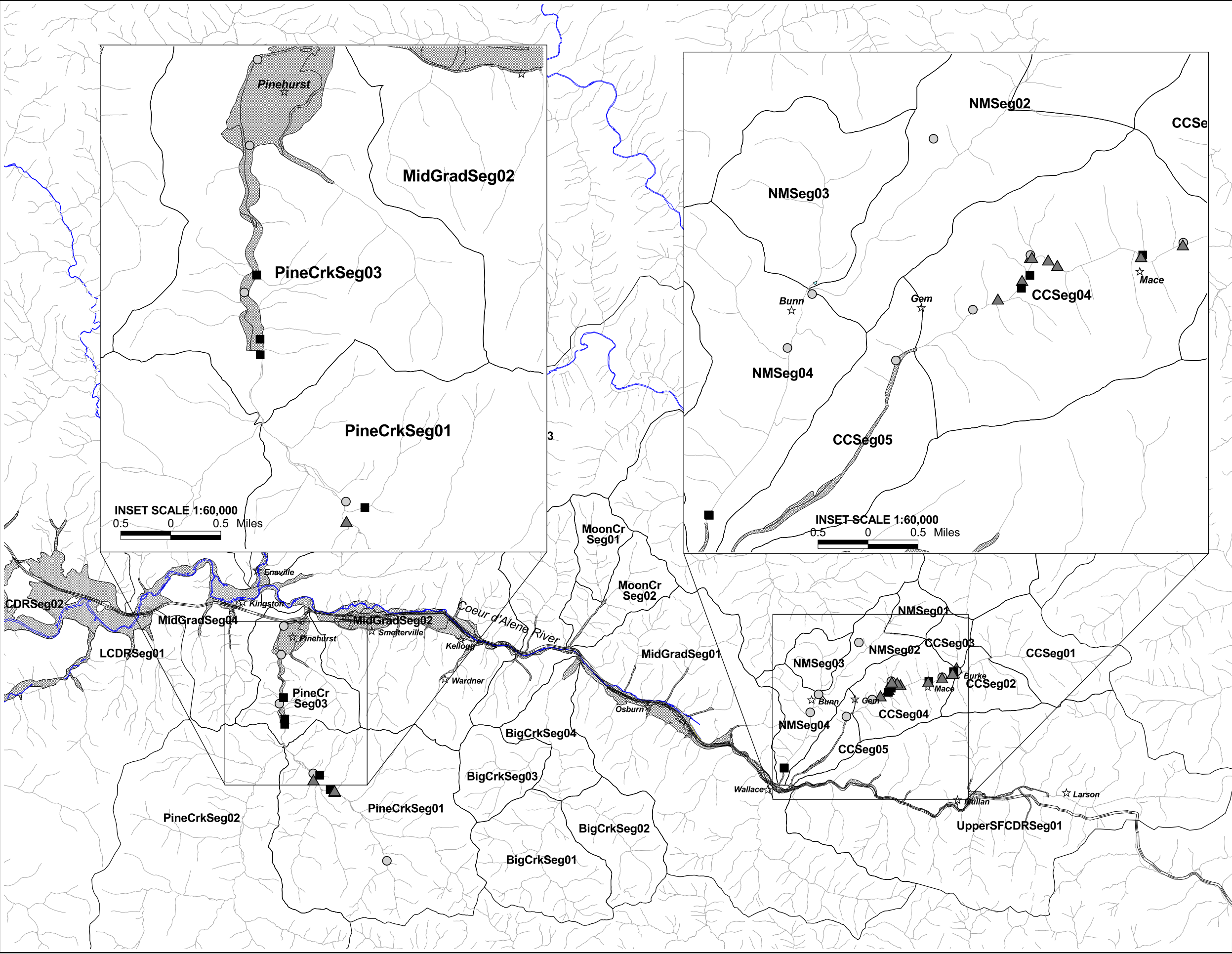


Doc Control Pending  
Generation 1  
n:\Projects\ri\_fs\ph\_ri\_geochem.apr  
VIEW: pH  
INSET ninemile et al inset  
LAYOUT: pH Surface Water  
10/13/2000

This Map is based on Idaho  
State Plane Coordinates West Zone,  
North American Datum 1983  
Date of Plot: OCTOBER 13, 2000



Figure G.5-3  
pH Values Found in Subsurface Waters



**LEGEND**

**pH Range**

- 5.1-6.53
- ▲ 6.53-7.01
- 7.01-8.66

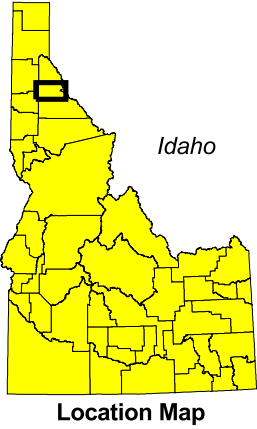
Stream

Interstate 90

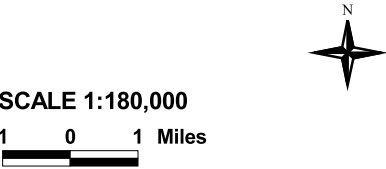
City

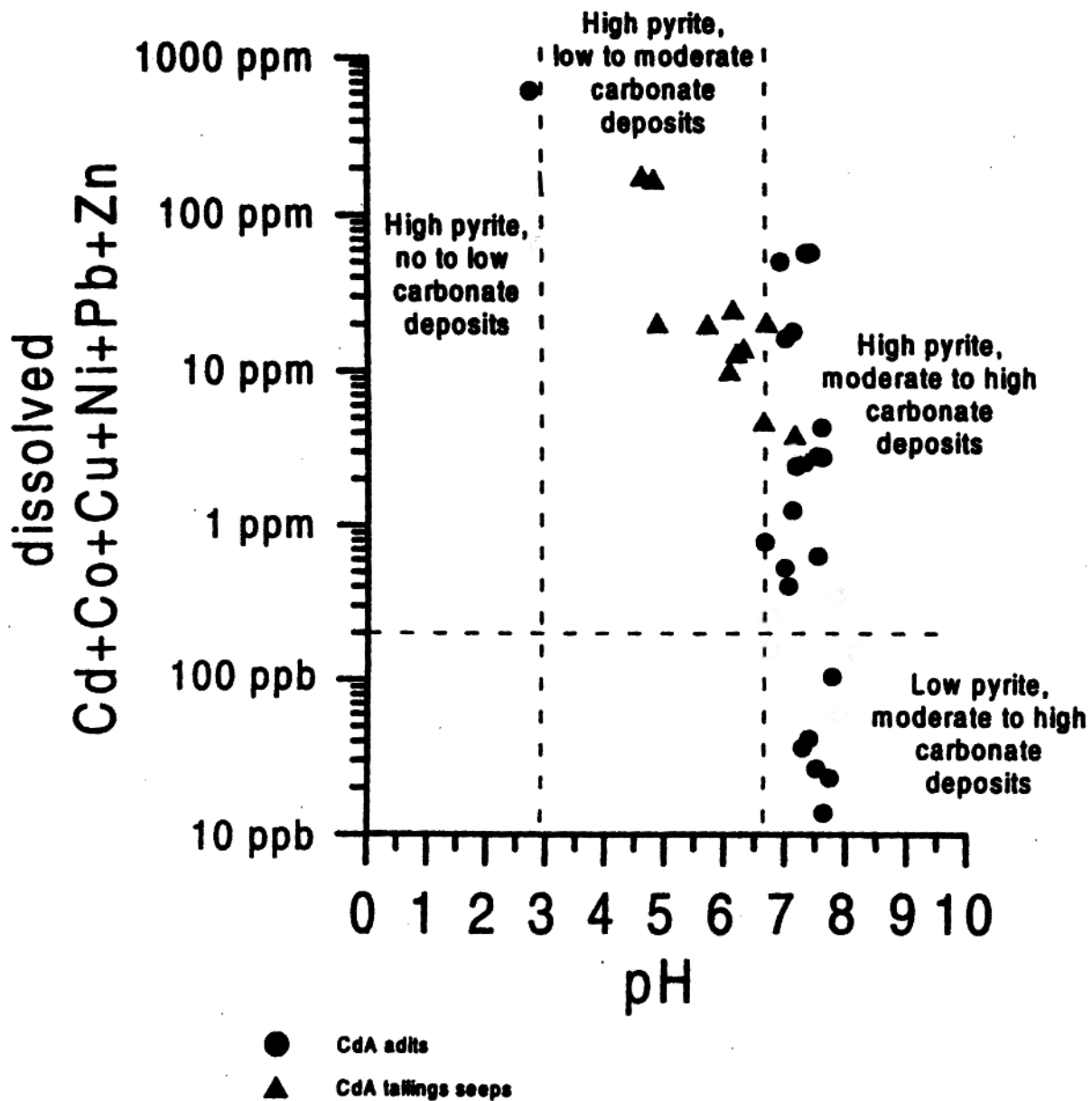
River Segment Boundary

River/Lake/Floodplain



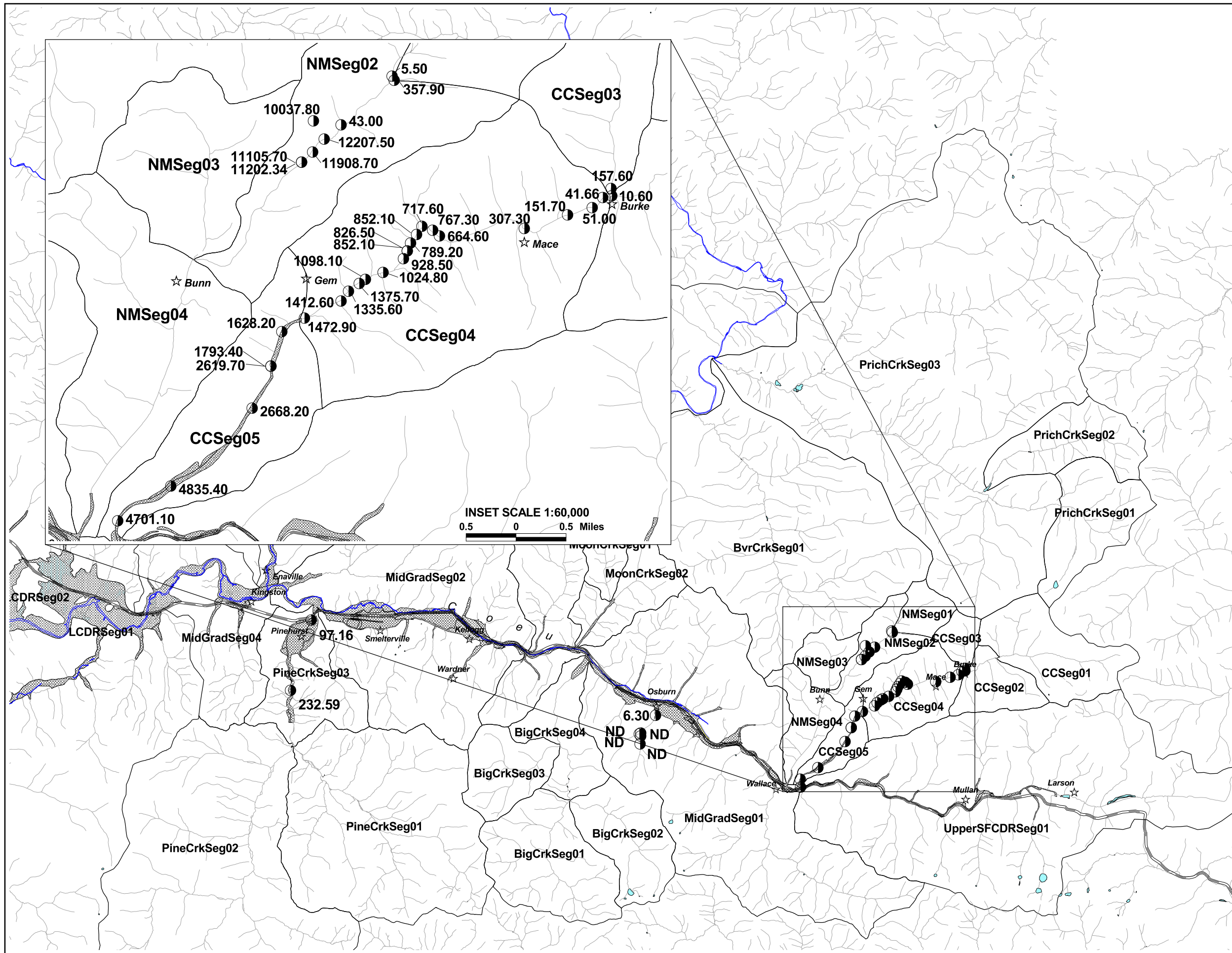
- NOTES**
- 1) Base map coverages obtained from the Coeur d'Alene Tribe, URS Greiner, Inc., CH2M HILL, and the Bureau of Land Management.
  - 2) Sampling locations obtained from URS Greiner, Inc., Technical Data Management database as of 10/16/99.





From Balistrieri 1999

Figure G.5-5  
Total Dissolved Metal  
(Pb+Zn+Cd+Cu+Co+Ni) Concentrations (µg/L)  
Found Throughout the Coeur d'Alene Basin



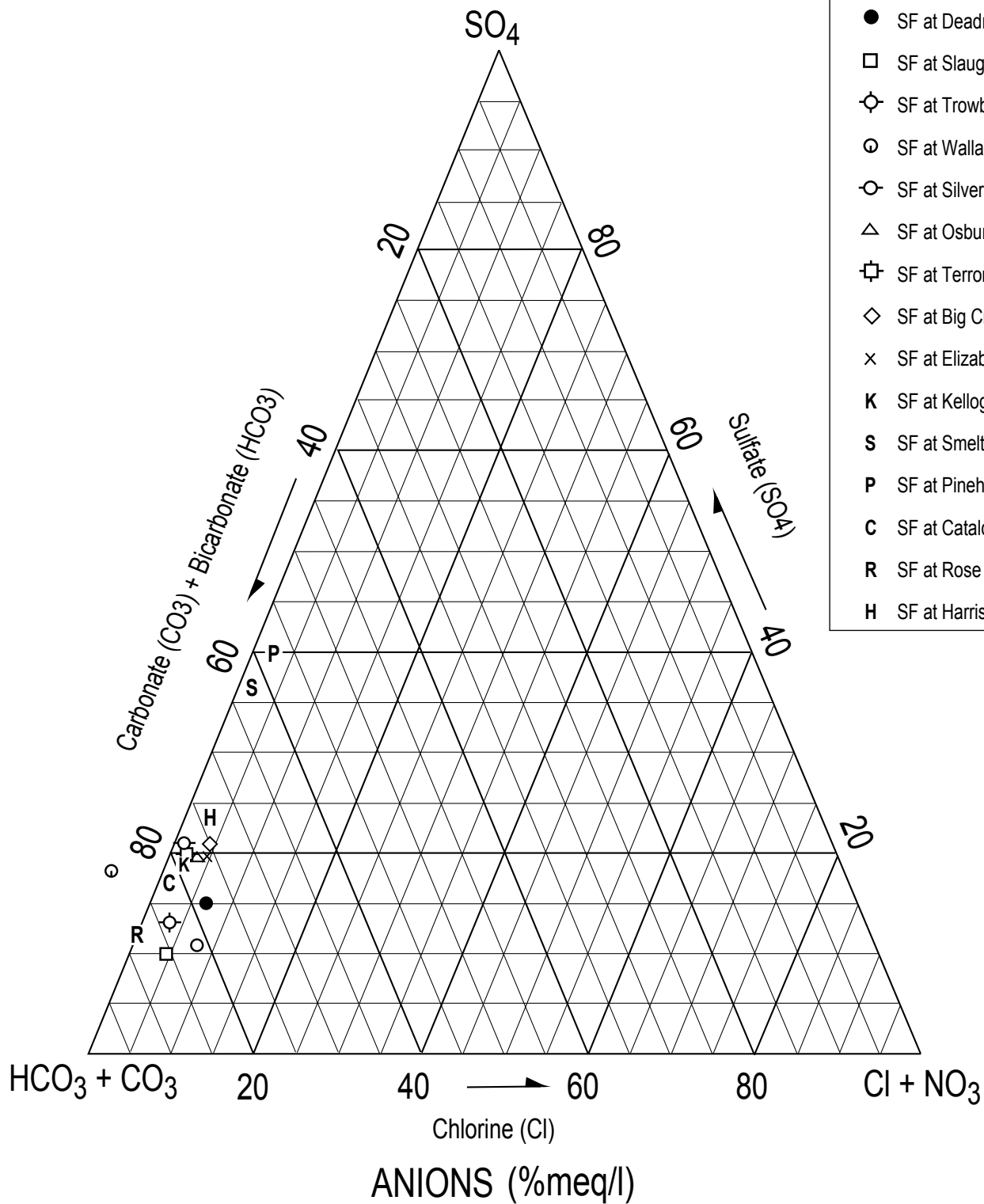
027-RI-CO-102Q  
Coeur d'Alene Basin RI/FS  
RI REPORT



Doc Control Pending  
Generation 1  
n:\Projects\ri\_fs\ph\_ri\_geochem.apr  
VIEW: Total dissolved metals  
INSET VIEW: totals inset  
LAYOUT: total dissolved metals  
10/13/2000

This Map is based on Idaho  
State Plane Coordinates West Zone,  
North American Datum 1983  
Date of Plot: OCTOBER 13, 2000





LEGEND	
○	SF at O'Brien
●	SF at Deadman
□	SF at Slaughterhouse
⊕	SF at Trowbridge
⊙	SF at Wallace
⊖	SF at Silverton
△	SF at Osburn
⊞	SF at Terror Gulch
◇	SF at Big Creek
×	SF at Elizabeth Park
K	SF at Kellogg
S	SF at Smelterville
P	SF at Pinehurst
C	SF at Cataldo
R	SF at Rose Lake
H	SF at Harrison

Note: Data Obtained From a High-Flow Sampling Event (Woods 2000)



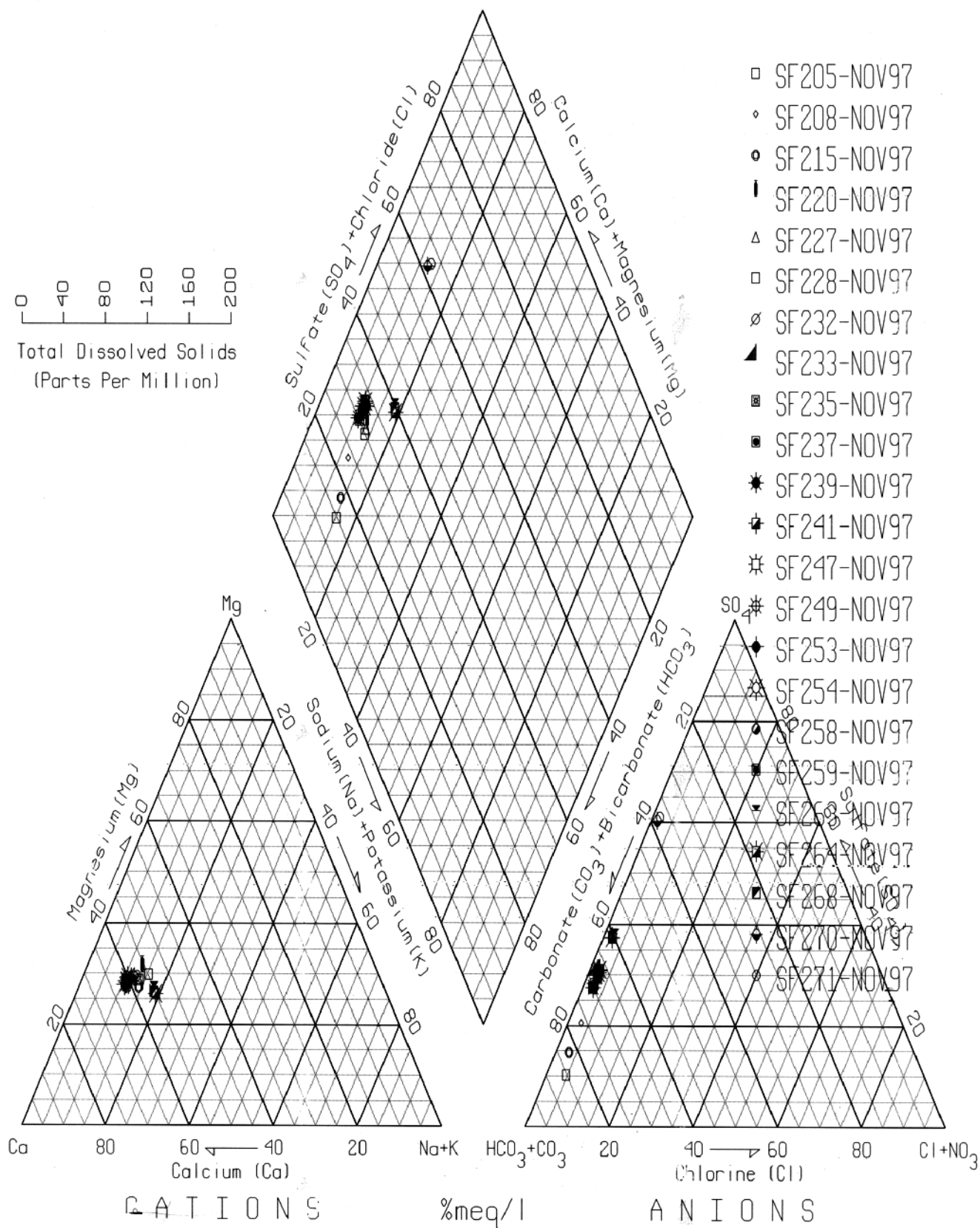
027-RI-CO-102Q  
Coeur d'Alene Basin RI/FS  
RI REPORT

Doc. Control:  
Generation: 1

IN-113  
062200

**Figure G.5-6**  
**Water Types on the South Fork and Main Stem of the**  
**Coeur d'Alene River - High Flow**

0 40 80 120 160 200  
Total Dissolved Solids  
(Parts Per Million)



Note: Data Obtained From a High-Flow Sampling Event (Woods 2000)

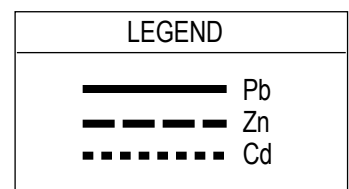
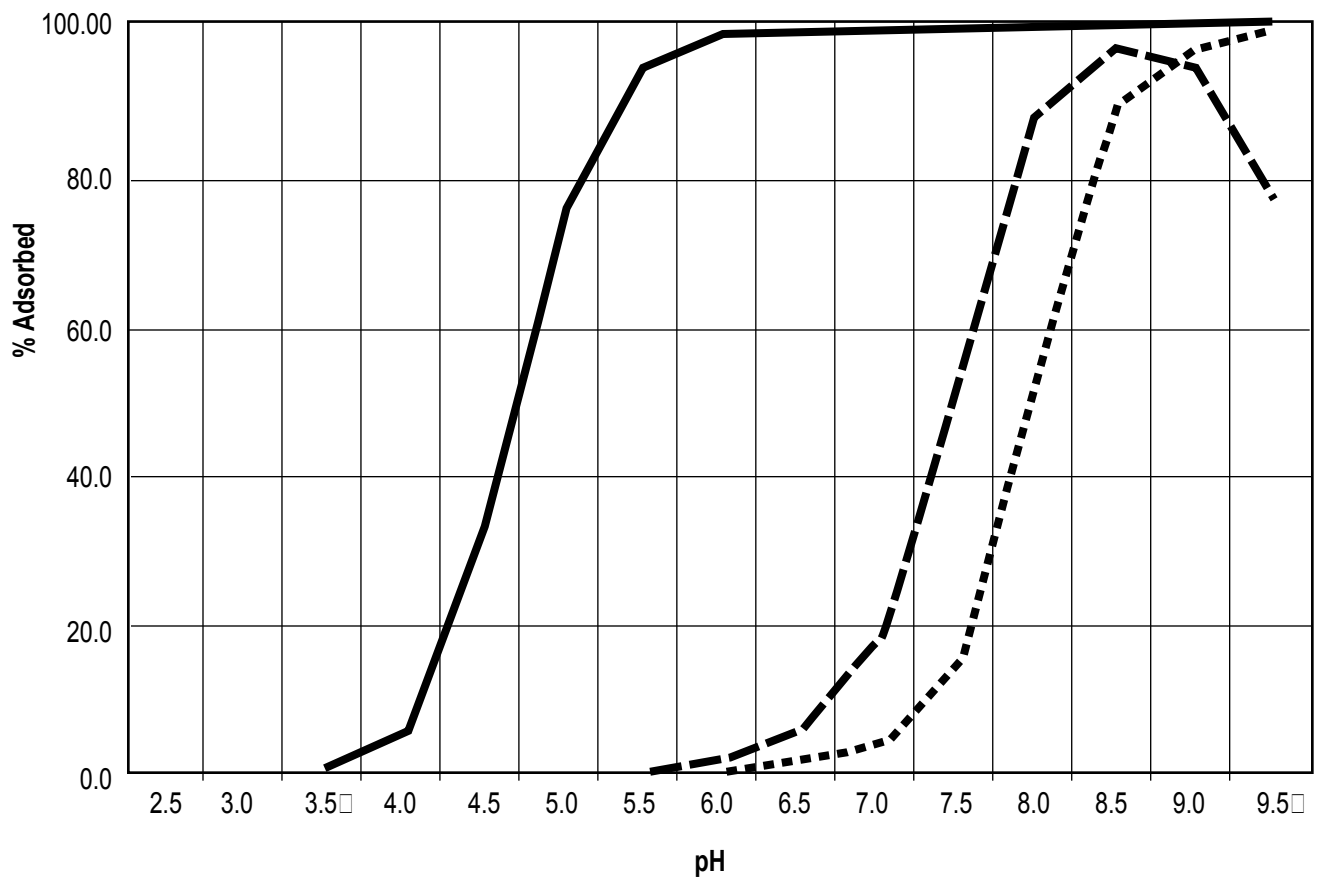


027-RI-CO-102Q  
Coeur d'Alene Basin RI/FS  
RI REPORT

Doc. Control:  
Generation: 1

IN-1133  
062200

**Figure G.5-7**  
**Water Types on the South Fork CDR and Main Stem of the**  
**Coeur d'Alene River - Low Flow**



**Table G.5-1**  
**Correlation Coefficients (r-values) for a High-flow Event**

	<b>Total Fe</b>	<b>Total Pb</b>	<b>Total Zn</b>	<b>Total Cd</b>	<b>Total Mn</b>	<b>pH</b>
Total Fe	1.00	0.62 (0.97)	0.42 (0.95)	0.21 (0.93)	0.78	0.03
Total Pb		1.00	0.73	0.45	0.71	-0.16
Total Zn			1.00	0.74	0.45	-0.32
Total Cd				1.00	0.27	-0.24
Total Mn					1.00	0.08
pH						1.00

Source: 1999, URS 2000.

**Table G.5-2**  
**Correlation Coefficients for a Low-flow Event**

	<b>Total Fe</b>	<b>Total Pb</b>	<b>Total Zn</b>	<b>Total Cd</b>
Total Fe	1.00	0.15	-0.07	-0.09
Total Pb		1.00	0.76	0.80
Total Zn			1.00	0.98
Total Cd				1.00

Source: November 1997, URS 2000.

**Table G.5-3**  
**Predicted Versus Measured Adsorption of Lead, Cadmium,**  
**and Zinc During a Low-flow Event**

Location	Percentage of Metal Found in Particulate Form - Fall 1997 Predicted and Measured					
	Lead (%)		Cadmium (%)		Zinc (%)	
	Predicted	Measured	Predicted	Measured	Predicted	Measured
SF205	89.7	63	6.7	42	33.2	63
SF208	81.4	69	1.3	42	9.5	59
SF215	4.2	98	0.0	99	0.0	60
SF220	33.6	63	0.2	0	1.7	8
SF227	38.7	63	0.3	0	2.4	2
SF228	74.4	67	1.4	1	10.5	14
SF232	14.8	35	0.0	0	0.2	6
SF233	5.8	30	0.0	0	0.0	6
SF235	1.6	57	0.0	0	0.0	0
SF237	10.6	34	0.0	0	0.2	0
SF239	11.5	51	0.0	0	0.1	2
SF241	4.2	50	0.0	0	0.0	2
SF247	1.8	33	0.0	0	0.0	5
SF249	18.5	36	0.1	0	0.8	0
SF253	17.2	28	0.3	0	2.1	8
SF254	13.7	28	0.1	0	0.7	6
SF258	13.3	29	0.1	0	0.5	7
SF259	55.0	25	0.1	0	0.8	7
SF263	33.9	29	0.3	0	2.7	0
SF264	17.9	27	0.1	0	0.8	2
SF268	15.5	32	0.0	0	0.3	0
SF270	63.4	59	1.0	0	7.6	5
SF271	64.3	87	0.6	0	4.7	8

**Table G.5-4**  
**Predicted Versus Measured Adsorption of Lead, Cadmium,**  
**and Zinc During a High-flow Event**

Location	Lead (%)		Cadmium (%)		Zinc (%)	
	Predicted	Measured	Predicted	Measured	Predicted	Measured
SF650	98.9	100.0	NA	ND	81.3	91.1
SF205	98.9	100.0	NA	ND	31.9	83.3
SF208	98.6	100.0	NA	ND	30.5	82.5
NF50	98.0	100.0	NA	ND	5.2	75.5
SF271	98.7	99.4	10.4	70.0	48.4	66.1
LC50	93.4	98.6	1.5	100.0	10.8	68.1
LC60	94.9	95.3	1.7	100.0	12.6	62.5
SF249	94.7	99.1	2.8	60.0	18.8	64.8
SF253	96.9	98.8	12.0	52.5	52.7	52.6
SF239	97.7	99.0	6.7	62.5	36.9	60.8
SF259	99.8	99.2	89.9	66.7	98.3	61.9
BC260	99.4	100.0	NA	ND	36.9	98.0
SF655	98.9	99.4	21.7	62.5	69.2	72.1
SF268	98.8	99.1	16.8	65.0	62.0	69.3
SF270	99.9	0.0	64.7	15.0	93.0	12.8
PC315	97.9	100.0	NA	ND	30.5	50.0
SF233	98.7	98.2	20.1	40.0	66.4	43.0
NM305	91.4	97.1	1.2	27.8	9.0	34.6
CC288	97.9	98.7	6.6	47.3	36.6	52.1